Feature article

Analysis of spherical indentation of porous ceramic films

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ABSTRACT

Spherical indentation of a porous brittle La0.8Sr0.2Co0.2Fe0.8O3 ceramic film (porosity = 39.7%) on a stiffer elastic Ce0.5Gd0.4O1.95 substrate is simulated by finite element modelling incorporating the Gurson model to account for densification. The simulated load-displacement curves, apparent elastic modulus E, indentation hardness H and densification profile are all in good agreement with experimental data for the film. The simulations show that E and H are not sensitive to film residual stress. However E is very sensitive to the indent depth-film thickness ratio f, although H is less so for f < 0.3. The simulated dependence of E and H on f are highly consistent with experimental data, supporting the extrapolation of E and H measured for 0.1 < f < 0.3, to zero depth for good estimates of the film-alone properties. The inclusion of densification in the simulation makes only a small difference to E, but has a large influence on H as a function of indentation depth.

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1. Introduction

The rapid development of porous thin ceramic films, which are indispensable for applications in filters, sensors and energy conversion technologies [1–3], has led to increasing advances in techniques for characterising their properties. The successful application of such materials relies heavily on their long-term mechanical stability and reliability. Porous thin ceramic films not only behave mechanically very differently from their isotropic dense film counterparts, but also can have significantly different microstructures and properties (such as mechanical behaviour) from porous bulk materials due to the influence of the substrate.

There is considerable interest in the use of nanoindentation as a means for mechanical property characterisation of small volumes of material [4], particularly for the measurements of elastic modulus and hardness of thin films on substrates. However, complexity and difficulties often arise in the deconvolution of film properties from the composite film/substrate response due to a combination of effects such as the substrate stiffness [5,6], residual stress in the film [7–9], indentation depth relative to film thickness [10,11] and film roughness [12,13]. Mechanical properties such as elastic modulus, hardness and fracture toughness have been widely studied for dense ceramic films, using the nanoindentation technique.

When a porous brittle film is used an additional effect must also be considered, namely the collapse and densification of the porous microstructure upon indentation [11].

In our previous studies, we have investigated the elastic and plastic deformation, and fracture, using spherical indentation in a porous bulk ceramic (La0.8Sr0.2Co0.2Fe0.8O3, LSCF, used in many solid oxide fuel cells) with a wide range of porosities (4–45%) [14,15]. A spherical indenter was preferred to a sharp indenter (Vickers or Berkovich) because even at shallow indentation depth a volume of material can be sampled that is sufficiently large to include a large number of ceramic grains. These studies showed how collapse and densification under the indenter influences the measurement of mechanical properties by spherical indentation and also how these phenomena can be incorporated satisfactorily into finite element modelling (FEM) using the Gurson material model to describe the densification process. In the present study, we extend these experiments and simulations to porous ceramic films on dense substrates. It is found that the apparent elastic modulus of porous thin ceramic films deposited on dense substrates is affected by the substrate at ratios of depth to film thickness similar to those established for dense films.

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2. Experimental and simulation procedures

2.1. Indentation experiments

Porous LSCF layers deposited on dense Ce0.9Gd0.1O1.95 (CGO) substrates were prepared by tape casting and high temperature sintering at 1000 °C to give films with 39.7% porosity. Nanoindentation experiments using a spherical diamond indenter (25 μm radius) were conducted at peak loads of up to 500 mN. The densified region reached the substrate when the penetration depth was approximately 2 μm and this was chosen as a base case in the simulations. Detailed description of the specimen preparation and indentation experiments can be found in [11]. The apparent elastic modulus and indentation hardness were calculated using the method of Oliver and Pharr [4]. As in our previous work on bulk porous LSCF specimens [14,15], the surface and cross-sectional microstructures, including particularly the indentation-induced “plastic zone”, of the specimens were investigated using the FIB-SEM slice and view technique.

2.2. Finite element modelling

2D axisymmetric FE models for simulating indentation of the layered specimens were implemented in a similar way to those used for simulating indentation of bulk specimens described previously. The Gurson model was used to simulate the collapse and densification of the porous LSCF layers under the indenter. A number of indentation characteristics, such as the load-displacement curves, densification of microstructures, residual deformation profiles, were taken into account to justify the applicability of the model [14], as also performed for some other models in the literature [16,17]. Fig. 1 shows schematics of the modelling configuration in Abaqus CAE 6.12 (Dassault Systemes, USA), in which a thin layer of a homogeneous material, with effective properties the same as the porous layer, was built on the substrate with its top surface in contact with the tip of a rigid spherical indenter.

As for the bulk simulations [14], axisymmetric boundary conditions were imposed such that the nodes on the left edges of the layer and substrate, and the bottom edge of the substrate, were constrained. Only vertical displacement was allowed for the indenter. The film/substrate interface was defined as being perfectly bonded (i.e. no delamination or slippage can occur). Residual stresses in the deposited films could affect the indentation response and the resulting extraction of mechanical properties of the porous layer from the indentation curves. The simulation therefore incorporated an initial equi-biaxial in-plane residual stress in the deposited films as required. The interaction between the indenter tip and the top surface was set to be friction-free [18–20]. The materials were assumed to be homogeneous and isotropic and the substrate to have perfect elastic behaviour.

An adaptive meshing method was applied to generate meshes in the simulations such that areas close to the indenter had much higher element density than more remote regions. The element density progressively reduced, with increasingly coarse size, towards the far field domain. The complete meshing process is described in [14]. The loading and unloading of the indenter were simulated by vertical displacement of the indenter, as shown in Fig. 1(b) and (c). The input material properties are elastic modulus, $E$, Poisson’s ratio, $\nu$, Gurson yield stress and porosity for the porous film and the elastic modulus and Poisson’s ratio for the substrate. As discussed in our earlier work [14] the Gurson yield stress used in the simulations should be regarded only as a fitting parameter and does not equate to the yield stress of the dense matrix material as in the strict use of the Gurson model. However, it can be used to estimate the uniaxial yield stress of the porous material [14]. The classical theory relating hardness to yield stress for metals [21] no longer applies for the porous ceramics, as yielding does not occur at a constant shear stress, nor at a constant volume [22]. Nevertheless, our previous results [14] on a series of porous LSCF bulk materials containing different levels of porosity showed a similar relationship between the uniaxial yield stress of the porous medium and the value of its indentation hardness. The effect of the input Poisson’s ratio on the mechanical properties was also examined for the bulk materials and the result showed negligible influence [14]. A value of 0.3 was used in the simulations. The apparent elastic modulus and the indentation hardness were calculated from the simulated indentation curves using the same method as used for analysing the experimental data.

3. Results and discussion

3.1. Influence of residual stress

The first investigation was to examine, using the simulation, how the indentation curves and extracted material parameters would be influenced by a pre-existing residual stress in the film. This was done by first fitting a simulated curve to an experimental one as a base case to obtain material parameters for the film. The base case simulation was then run with a range of values for the residual stress, but keeping all other data input constant. The fitting procedure adopted was based on that described previously for bulk specimens [14]. In summary it involved making initial estimates for the film material parameter values and then refining them so as to reproduce the experimental indentation curve with empha-
sis on matching the displacement depth at peak load, which gives the indentation hardness, and the initial unloading stiffness, which determines the apparent elastic modulus when analysed using the conventional method. The residual stress in the LSCF film is caused by the thermal mismatch between the film and the CGO substrate during cooling. In earlier work the room temperature residual stress in a film sintered at 1000 °C was measured using the X-ray diffraction technique to be 100 MPa in equi-biaxial tension (in the plane of the film) and is lower than that expected from assuming elastic behaviour during cooling from the fabrication temperature due to some stress relief [7]. Therefore, indentation simulations were performed with a series of residual stress values ranging from 0 to ±300 MPa as the initial stress state of the film.

The simulation input parameters that gave the best fit to the base case indentation curve are listed in Table 1. The elastic modulus of the substrate was 190 GPa.

Table 1
| Porosity (%) | Elastic modulus (GPa) | Gurson yield stress (GPa) | Thickness (µm) | Measured residual stress (MPa) |
|--------------|-----------------------|--------------------------|----------------|-----------------------------|
| 39.7         | 48.3 [11]             | 0.97                     | 10             | 100 ± 2                     |

Fig. 2 shows the simulated indentation response curves for a range of initial residual stresses, keeping all other input parameters constant, compared with one of the actual typical experimental curves. The results in Fig. 2 shows that the initial residual stress in the film has only a small effect on the indentation response, and the base case simulation agrees well with the experimental indentation curve. The increase of residual stress from 0 to 300 MPa did not change the plastic indentation depth much as shown in Fig. 2. The irregularity in the experimental loading response, marked by a dotted oval in the figure, is thought to be caused by some local heterogeneity in the microstructure of the porous film. Similar irregularity was observed in other tests. For clarity, only one data set is shown in the figure. It should be noted that the slightly wavy nature in the loading parts of the simulated curves is not due to the finite mesh size, but is caused by the iteration procedure that matches the plastic and elastic regions when using the Gurson model, as reported in our earlier paper [14].

Fig. 3 shows the simulation results for the distribution of porosity in the film in the “plastic zone” under the indenter with different levels of initial residual stress. In the Gurson model the yield condition is given by

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

where $f$ is the porosity, $\sigma_y^f$ is the Gurson yield stress of the dense matrix material (dense LSCF in this case), $q$ is the effective von Mises macroscopic stress and $p$ is the macroscopic hydrostatic stress. For each volume element at a given increment in displacement of the indenter, the plastic strain due to 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.

As can be seen from Fig. 3, the residual porosity close to the contact with the indenter was sensitive to the residual stress and dropped from 22.0% to 11.4% as the residual tensile stress increased from 0 to 300 MPa. A significant difference can also be observed in the porosity contour plots in Fig. 3(a)–(c), as a lower residual stress resulted in a smaller porosity gradient along the central axis but broader porosity distributions elsewhere. The increase of residual tensile stress facilitates pore-filling densification by opening the original structure, particularly in the region directly underneath the indenter tip (Fig. 3(b)). In Fig. 3(d) a slight change in porosity at 10 µm (i.e. the interface of film and substrate) with residual stress can be seen and is caused by the densification zone reaching the film/substrate interface.

Despite the overall lack of sensitivity of the indentation curves to the residual stresses, they may nevertheless have a significant influence on the apparent measured mechanical properties of the films. This has already been observed for measurements of fracture toughness using sharp indentation as reported in [7]. It is possible that the residual stress also has an influence on the apparent elastic modulus and hardness measured using indentation. To explore this, the simulated indentation curves were analysed in the same way as experimental ones to extract values for the apparent elastic modulus and indentation hardness. The results are presented in Fig. 4 and shows that the apparent elastic modulus and hardness are both relatively insensitive to the residual stress. When the residual stress varies from −300 MPa (compressive) to 300 MPa (tensile), the apparent elastic modulus increases by 1.5% and the indentation hardness decreases by 1.3%. However, the apparent elastic modulus (= 76.9 GPa) is much greater than the true input elastic modulus for the film (48.3 GPa) due to the effect of the substrate, which will be discussed later.

3.2. Densification under the indenter

3.2.1. Simulation compared with experiment

The indentation-induced densification zones predicted by simulation (Fig. 3(a)–(c), with different levels of residual stress included in the films) indicate that the boundary of the densification zones almost reaches the interface, and is approximately 5 times the indentation depth. Fig. 5 shows the indentation deformation in the experiment revealed using the FIB-SEM cross section technique. No detectable plastic deformation of the substrate is evident. The cross-sectional densification regions found experimentally and in the FEM simulation (Fig. 3(b)) both show very similar parabolic-shaped profiles. Furthermore, no pile-up or sink-in is seen in the...
3.2.2. Porous film compared with porous bulk

The indentation response and densification behaviour of a porous bulk sample (200 μm thick) with identical initial porosity to the porous film, but zero residual stress, was also simulated and compared with the behaviour of the film. The same material input parameters were used for both the bulk and the film and the simulations were carried out with the same maximum penetration depth (the experimental value) for both bulk and film. Fig. 6 shows the resulting response curves and the calculated residual porosity close to the contact with the indenter.

Fig. 6(a) shows that the indentation loading curve is slightly different for the bulk and film simulations, and that a smaller load was needed for the bulk to reach the same indentation depth which corresponds to a lower hardness. However, there is a large difference in the unloading curves in that the bulk has a much smaller unloading stiffness, resulting in smaller apparent elastic modulus (48.8 GPa). This is due to the influence of the substrate in the case of the film and will be discussed in more detail later. Compared with the bulk, the indentation-induced densification is more noticeable experimental or simulation results, and no delamination can be detected in the film/substrate interface in Fig. 5.

Fig. 3. Simulation results for a film after indentation showing contour plots of the distribution of volume fraction of porosity (a) with zero residual stress, (b) with 100 MPa residual tensile stress, and (c) with 300 MPa residual tensile stress and (d) the variation of residual porosity along the central line under the indenter with different residual tensile stress incorporated in the film (0–300 MPa).

Fig. 4. Apparent elastic modulus and indentation hardness derived from the simulations as a function of residual stress in the film (negative values mean the stress is compressive).
in the films (Fig. 6(b)). The lowest value of porosity just under the indenter is 19.0% for the film compared with 22.5% for the bulk. This is mainly due to the residual tensile stress in the base case simulation for the film. When the residual tensile stress is zero, the difference becomes negligible as seen in Fig. 6(b) (22.5% for the bulk compared with 22.0% for the film).

### 3.3. Effect of film thickness on indentation response

FEM simulations were carried out for a range of film thickness values in the base case, (i.e. with a constant maximum indentation depth of 1.97 μm and residual stress of 100 MPa) to study the effect of film thickness on the indentation response and the resulting values of apparent elastic modulus and hardness. The results are presented in Fig. 7 and shows that there is very little influence for film thickness greater than approximately 20 μm, as a result of diminished influence from the substrate. In this region the ratio of indentation depth to film thickness falls below 10%, consistent with the conventionally accepted rule of thumb for indentation of thin films in order to avoid significant substrate influence. Below approximately 20 μm, however, the stiff substrate has an increasing effect as the film becomes thinner, as expected qualitatively. The densification under the indenter (Fig. 7(b)) is more severe when the film thickness is below 10 μm. As an example, for a film thickness of 5 μm the porosity immediately under the indenter is reduced to only approximately 6.9%. The results in Fig. 7 also shows that the porosity maintained its initial value only at depths larger than 10 μm in films thicker than 10 μm. Fig. 7(c) indicates that the apparent elastic modulus is very sensitive to the film thickness in films thinner than 20 μm, whereas the indentation hardness is much less sensitive. This is expected because the elastic field has longer range than the plastic field. It is also likely that the effect on apparent elastic modulus is underestimated in these simulations of porous films as the Gurson model does not take into account the effect of densification in increasing the local elastic modulus i.e., it assumes that elastic modulus is independent of porosity in the densified regions, which will not be true in reality.

### 3.4. Effect of indentation depth

The FEM simulation was used to explore the influence of indentation depth at constant film thickness by varying the indentation depth in the base case. These were performed because they are directly comparable with experimental data [111]. The results were similar to the ones in which the film thickness was varied at constant maximum indentation depth, since the main controlling parameter is expected to be the ratio of maximum indent depth to film thickness, as verified in Fig. 8. The simulation results for the apparent elastic modulus and indentation hardness are compared with the experimental results in Fig. 9.

The initial strong increase of the experimental data (below 5% of the film thickness) is due to the surface roughness features in the actual films which causes non-ideal initial contact. This roughness effect was not taken into account in the FEM, so that the results from simulation over this range of indentation depth (0–5% of film thickness) deviate significantly from the experimental results. For indentation depths between 5% and 30% of film thickness it is seen that the results from FEM simulations agree very well with the experimental results. In our previous study [111] we suggested that extrapolation to zero depth of the apparent elastic modulus and indentation hardness results, obtained between 10 and 20% of the film thickness, should be considered as providing the true values for the film as recommended for sharp indentation of dense films in the ISO 14577 standard testing procedure. The present simulation results show that this is a reliable procedure for the porous films. For indentation depths greater than approximately 30% of the film thickness the experimentally measured apparent elastic modulus

![Comparison of (a) indentation response curves and (b) porosity change along the axis under the indenter after indentation for bulk and film (with two values of residual stress) using the same material parameters and maximum indentation depth.](http://dx.doi.org/10.1016/j.jeurceramsoc.2016.10.002)
and indentation hardness begin to exceed those derived from the simulations. In particular, the apparent elastic modulus from the simulations does not tend to the expected asymptotic value for the substrate (190 GPa) as quickly as observed in the experiments. This is probably mainly due to the deficiency in the Gurson model mentioned earlier in that it does not allow for an increase in the elastic modulus of the film in the densified region.

3.5. Influence of densification

In this section we explore how much the densification under the indenter affects the way in which the apparent elastic modulus and indentation hardness depend on indentation depth. In order to do this the Gurson model in the base case was replaced by the volume-conserving elastic-perfectly plastic material model for the film (von Mises model). The yield stress in this model was estimated from our previous study [14] of bulk material of similar porosity to be 1.75 GPa. The residual stress was unchanged. The results are shown in Fig. 10. It is seen that including densification has only a small influence on the apparent elastic modulus. This is because the elastic response is not sensitive to the details of deformation in the plastic zone and is dominated by longer range stresses and strains. On the other hand, the indentation hardness is much more sensitive to densification. In particular, when no densification is assumed,
the simulations (Fig. 10(b)) do not show a plateau in the region of shallow indentation which is a characteristic of the behaviour with densification. The increase in indentation hardness with depth in the case of the von Mises simulation is probably due to conservation of volume during plastic deformation leading to pile-up (hence a larger contact area than estimated in the analysis at a given load). Conversely, when densification occurs there is no pile-up and the plastic zone is more localised and therefore less influenced by the substrate.

4. Conclusions

The simulations have shown that using the Gurson model to describe densification under the indenter during spherical indentation of a porous ceramic film on a stiff substrate gives indentation curves and porosity distributions in good agreement with experiments, despite the fact that the Gurson model is strictly applicable to metals with less than approximately 15% porosity. However, in the current simulations the Gurson yield stress is not equal to the yield stress of the dense matrix material, but is regarded as an adjustable fitting parameter.

The simulations show that the details of the distribution of porosity in the densification zone depend on any residual stress in the film, but the apparent elastic modulus and indentation hardness are not sensitive to residual stress.

Simulations in which the film thickness and indentation depth were varied show that the apparent elastic modulus is very sensitive to the ratio of indent depth to film thickness, but that the indentation hardness is less so for depths less than 30% of the film thickness. The simulated dependence of apparent elastic modulus and indentation hardness with depth to thickness ratio are in good agreement with experimental data. They also support the procedure proposed previously whereby extrapolation of apparent elastic modulus and indentation hardness, measured in the depth range of 10 to 30% of film thickness, to zero depth in order to obtain good estimates of these parameters for the film alone.

Fig. 9. Comparison between experimentally measured apparent elastic modulus and indentation hardness and values extracted from FEM simulations, as a function of ratio of indent depth to film thickness for the actual LSCF films (sintered at 1000 °C) with the same porosity, thickness, residual stress and input mechanical properties [11].

Fig. 10. Influence of densification on the (a) apparent elastic modulus and (b) indentation hardness for the base case. The von Mises simulations were carried out with varying film thickness and constant maximum indentation depth.
The inclusion of densification in the simulation makes only a small difference to the apparent elastic modulus, but has a large influence on the indentation hardness as a function of indentation depth.

Although the experiments reported here are for a single ceramic material (LSCF), our earlier paper [14] gives experimental data for a range of porosities of this material and therefore the behaviour and model described should be generally applicable to porous ceramics formed by partial sintering of powder coatings.

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Appendix A. Supplementary data

Raw data on which this paper is based can be openly accessed at https://dx.doi.org/10.6084/m9.figshare.4007940.v1

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