A multi-scale model is presented for the evolution of microstructure, sintering and deformation of columnar EB-PVD thermal barrier coatings. Computational studies are presented of the sintering of a coating constrained by a rigid substrate. It is demonstrated that the sintering process can become unstable when the in-plane stiffness exceeds a critical value. Imperfections in the coating can develop into cracks, which propagate through the thickness of the coating, creating a pattern of “mud cracks”. The simulations have motivated the development of simplified models of this process which describe the sintering response and the development of mud cracks in terms of the evolution of a small number of degrees of freedom. These simple models capture the major features of the more detailed computational simulations. They also allow the conditions under which imperfections grow into cracks to be readily identified and predict a density of mud cracks that is consistent with experimental observations.

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1. Introduction

The thermal efficiency of a gas turbine engine is primarily governed by the turbine entry temperature (TET) of the gas into the engine. The TET of today’s gas turbine engines can be in excess of 1500 °C. This means that the hot-section components of the engine are required to operate in aggressive environments significantly in excess of their melting temperatures, requiring extensive cooling coupled with heat resistant and protective coatings. Although the highly loaded blades and vanes in the high pressure turbine (HPT) are heavily cooled, current substrate materials are unable to provide sufficient strength above 1500 °C (Peters et al., 1997). If a thermal barrier coating (TBC) is deposited on a superalloy turbine blade which is gas cooled, a substantial temperature drop of the order of 100–300 °C can be achieved at the metal surface (Belmonte, 2006). Use of thermal barrier coatings (TBCs) result not only in increased thermodynamic efficiency of the engine, but they also prolong the durability of hot-section turbine components.

TBCs comprise thermally insulating materials having sufficient thickness and durability that they can sustain an appreciable temperature difference between the load bearing alloy and the coating surface. Further improvements in TBCs will require a better understanding of the complex changes in their structures and properties that occur under operating conditions that lead to their failure. TBCs comprise several layers as shown in Fig. 1, with each performing a specific function and exhibiting markedly different properties. The primary layers are: the top coat, which provides thermal insulation; the superalloy substrate which carries the structural load; an aluminium containing bond-coat (BC) between the substrate and the TBC, which provides a surface to which the top coat can adhere; and a thermally grown oxide (TGO),
predominantly alumina, that forms between the top coat and BC and provides oxidation protection. Each of these elements is dynamic and all interact to determine the performance and durability. An expansion of the application of TBCs to more demanding scenarios requires that their basic thermo-mechanical characteristics be understood and quantified (Evans et al., 2001). Although failure prediction and performance improvements of TBCs requires a systems approach, there are critical issues closely related to the top coat and the bond-coat respectively. In this paper, we focus on the behaviour of the top coat.

In turbine applications the top coat is generally deposited using an EB-PVD process. The deposition conditions are designed to create a columnar grain structure (2–10 μm diameter) with multi-scale porosity. The disconnected columns impart ‘strain tolerance’ to the TBC because they can separate at high temperatures, accommodating thermal expansion misfit strains. At operating temperatures, the top coat will densify, driven by a reduction in surface energy associated with pores and surface features. This process is commonly referred to as sintering. Sintering in EB-PVD TBCs results in the partial healing of the gaps between columns and a reduction in porosity. This accelerates TBC failure by making the top-coat stiffer and less ‘strain tolerant’. It also results in an increase in thermal conductivity of the coating and higher substrate temperature (Zhu and Miller, 1998). The increased thermal cyclic stresses and accumulated sintering strains provide the major driving forces for shrinkage-cracking that originate at the TBC surface, eventually leading to TBC spallation (Zhu and Miller, 1999). The long-term thermal conductivity increase measured using laser conductivity tests is attributed to the sintering of both the inter-columnar and intra-columnar micro porosity (Zhu et al., 2001). It has been demonstrated that the strain tolerance in as-deposited samples decreases with an increase in deposition temperature (Wada et al., 2005).

Two factors influence the densification of a coating. One is the geometric constraint on the lateral shrinkage of the coating by the rigid alloy as the coating tries to densify to lower its overall internal surface area. This classical problem of constrained sintering was addressed initially by Bordia and Jagota (1993) for particulate ceramics. The other factor is the effect of stress produced by thermal expansion mismatch between the coating and alloy. Indeed, Lughi et al. (2004) demonstrated experimentally that thermal expansion mismatch is not the dominant factor in determining the densification behaviour of these coatings.

Wellman et al. (2004) studied the effect of TBC morphology, aging and sintering on the erosion rate of EB-PVD TBCs and found that the erosion rate decreases with decrease in column diameter, while thermal aging results in an increase of erosion rate, which depends on the aging temperature and time. Sintering enables cracks to propagate into neighbouring columns, as opposed to stopping at column boundaries and increases erosion rate (Wellman et al., 2004). In service, progressive sintering leads to build up of in-plane tension in the TBC. If the magnitude of this tension is sufficiently high it may lead to the formation of inter-columnar cracks in the coating. These cracks can propagate to the interface and lead to coating delamination and eventual spallation under thermal cycling (Clarke and Levi, 2003).

In this paper we focus on the sintering response of an EB-PVD top coat and examine the conditions under which inter-columnar cracks can develop within the coating. Hutchinson et al. (2006) have recently developed a micromechanical model for constrained sintering of EB-PVD TBCs and modelled the growth of tunnelling cracks in the coating by a cleavage mechanism. Here we explore an alternative mechanism of crack formation, which arises from instabilities in the sintering process. We rework the sintering model of Hutchinson et al. (2006) to provide a macroscopic sintering constitutive law, which we employ in a series of finite element calculations to evaluate the sensitivity of the sintering response to imperfections in the coating. The resulting simulations guide a series of simplified Rayleigh-Ritz models, which capture the major features of the growth of imperfections, and identify the conditions under which they develop into cracks.
2. Problem statement

The main objective of this paper is to identify the conditions under which mud cracks can develop in a thermal barrier coating. In service, a temperature gradient will exist across the coating. Here, however, we focus on the simpler problem of isothermal sintering as employed in the experimental study of Lughi et al. (2004). The methodology described here can be readily extended to non-isothermal situations, but it is important to fully understand the behaviour under isothermal first before addressing the full practical problem.

Following Hutchinson et al. (2006), we idealise the top coat as a regular array of parallelepiped columnar grains of square cross-section with dimensions $d \times d$, as illustrated in Fig. 2a. We describe the response in terms of a Cartesian co-ordinate system in which the $x_1$ and $x_2$ directions lie in the plane of the coating and are parallel to the sides of the columnar grains. The $x_3$ direction is perpendicular to the plane, with its origin at the interface with the substrate. The columns have a surface roughness of characteristic wavelength, $\lambda$. Asperities on the columns can come into contact. At elevated temperature, sintering occurs as a result of the diffusional flow of material away from the contact regions. This gives rise to macroscopic sintering strains, $\varepsilon_{11}^S, \varepsilon_{22}^S$. By considering the response of a representative volume element, we develop a constitutive model in Section 3 for the sintering rate in terms of the geometry of the internal contacts and the macroscopic stress experienced by the element. Finite element studies are undertaken of inter-columnar sintering of a constrained homogeneous film (Fig. 2a) and progressive sintering of a set of columns within a mud cracked square cluster of size $2R$ (Fig. 2b). These results are compared directly with the analyses of Hutchinson et al. (2006). We then use the model to evaluate the influence of imperfections (where the initial contact geometry of the asperities is slightly different to that experienced in the remainder of the coating) on the sintering process. This is conducted in 2 stages. First we model the evolution of microstructure for a set of arbitrary equi-spaced imperfections, see Section 4. We then consider the response for a square grid of imperfections, with the objective of identifying the conditions under which a square grid of cracks can develop from these initial imperfections, Section 4. The resulting mud cracked pattern is an idealisation of the patterns observed experimentally, for example by Lughi et al. (2004), see Fig. 2b. These simulations are used to guide the development of a two state variable Rayleigh-Ritz model, which we validate against the detailed finite element calculations, as described in Section 5. Use of this simpler model allows a wide range of geometric and material conditions to be evaluated and the conditions under which cracking occurs to be identified, but these calculations are unable to provide information about the average spacing of the mud cracks. This requires a three state variable model in which we follow the evolution of two families of imperfections. This is described in Section 6. In all the problems, the TBC layer is of height $H$ and it is assumed that the TBC film is perfectly bonded to the substrate.

![Fig. 2.](image-url)
3. Computational model

A representative macroscopic volume element of the coating is shown in Fig. 3. The element has a square cross section \( d \times d \), made up of 4 quarter columns which are in contact along lines that bisect the element along two mutually perpendicular planes, parallel to the \( x_1 \) and \( x_2 \) axes. The height of the element is equal to the wavelength \( \lambda \) of the undulations on the surface of the columns. Following Hutchinson et al. (2006), we assume that the elastic response does not depend on the detailed structure across the interface between the columns (the effect of asperity contact stiffness on the constitutive response is examined elsewhere (Kumar, 2010)). Inelastic deformation results from sintering and sliding between the asperities. We assume a simple linear viscous response for the sliding deformation. For the situations examined here the results are not sensitive to the magnitude of the viscosity. The inelastic strain-rates \( \varepsilon_{S11}, \varepsilon_{S22} \) arise from diffusional rearrangement at the asperity scale on two independent planes. We can therefore model these processes independently and superimpose the results to give the full constitutive response.

We assume simple shapes for the evolving asperities and develop the constitutive model within the framework of the variational principle described by Cocks et al. (1999) and Suo (1997). This requires an identification of the different contributions to the functional

\[
\Pi = \Psi + G
\]

where \( \Psi \) is a rate potential and \( G \) is the rate of change of Gibbs free energy of the system. Each of these quantities are expressed in terms of geometric rate quantities that describe the rate of evolution of the microstructure (i.e. the change in shape of the asperities). The most appropriate combination of rates is that which minimises the functional \( \Pi \).

We focus on the local sintering between contacting columns on a length scale \( \lambda \) (less than 1 \( \mu \)m) and neglect the much slower diffusion over larger length scales of the order of the column size \( d \) (2–10 \( \mu \)m) and column height \( H \) (100–200 \( \mu \)m). Consequently, we can solve for the evolution of the sintering strains \( \varepsilon_{S11} \) and \( \varepsilon_{S22} \) in the \( x_1 \) and \( x_2 \) directions respectively under fixed temperature \( T \).

3.1. Contact geometry

Consider the situation where the element of Fig. 3 is subjected to a stress \( \sigma_{11} \). Following Hutchinson et al. (2006), we associate all the surface roughness with one of the contacting surfaces, while the other surface is treated as perfectly flat. We assume the idealised saw-toothed contact geometry shown in Fig. 4. It proves convenient to define a reference configuration as illustrated in Fig. 4a. Note that the reference configuration is introduced for algebraic convenience only and may not be realised in practice. The geometry of the contacting asperities at a given instant can be characterised by the geometric parameters \((u_1, w_1)\) as shown in Fig. 4b. This simplification of contact geometry allows us to reduce the
number of independent geometric variables and to formulate an analytical micromechanical model for the evolution of contact geometry. The as-deposited columns of an EB-PVD coating have a highly irregular rough surfaces consisting of feathery arms Lughi et al. (2004). This surface roughness is smoothed within a few hours at the operating temperature as reported by Lughi et al. (2004), giving a surface profile that is reasonably well approximated by that of Fig. 4, with a wavelength $\lambda$ of the order of the spacing of the feathery arms in the as-deposited coating. As sintering proceeds, the contact width $2b_1$ increases and the combined peak-to-peak amplitude of the undulations $w_1$ decreases, while the wavelength $\lambda$ remains the same.

The objective is to solve for the local evolution of surface profile as characterised by $(u_1, w_1)$ due to the interfacial diffusion of matter from the contacts into the gaps of peak-to-peak amplitude $w_1$. Interfacial diffusion is driven by the combined driving forces of the net reduction in interfacial energy, and the change in potential energy of the system. Hutchinson et al. (2006) observed that the asperity profile angle $\beta$ quickly evolves to a constant value for a wide range of material and geometric parameters. They demonstrate that the steady-state angle $\beta$ is when $\partial G/\partial w_1 = 0$ and that it can be expressed in terms of the interface energy $\gamma_s$ and surface energy $\gamma_b$.

$$\beta = \cos^{-1}\left[\frac{1}{4} \left(\frac{\gamma_b}{\gamma_s} - 1\right) + \sqrt{\left(\frac{\gamma_b}{\gamma_s} - 1\right)^2 + 8}\right]$$  \hspace{1cm} (2)

Adopting this equilibrium asperity profile angle $\beta$ for the contact geometries, we can express all the geometric variables that define the contact geometry $(b_1, w_1, l_1)$ as a function of $u_1$

$$b_1 = \frac{\lambda}{2} \frac{1}{2} \sqrt{\lambda^2 - 4\lambda u_1 \cot \beta}; \quad w_1 = \frac{\tan \beta}{2} \sqrt{\lambda^2 - 4\lambda u_1 \cot \beta}; \quad l_1 = \frac{\sec \beta}{2} \sqrt{\lambda^2 - 4\lambda u_1 \cot \beta}$$  \hspace{1cm} (3)

i.e. the full sintering response can be expressed in terms of the evolution of a single geometric parameter, $u_1$.

The macroscopic sintering strain in the $x_1$ direction $\varepsilon_{11}^s$ can also be expressed in terms of the state variable $u_1$ (Hutchinson et al., 2006)

$$\varepsilon_{11}^s = \frac{u_1^0 - u_1}{d}$$  \hspace{1cm} (4)

Note that $u_1^0$ is the initial value of state variable $u_1$. As the asperities flatten during the sintering process, $u_1$ increases in magnitude and the centre-to-centre spacing of the columns decreases, giving rise to a negative (compressive) sintering strain.

3.2. Local sintering at contacts

At all contacts between columns, it is assumed that matter diffuses along the interface from the contacts, labelled $OA$ in Fig. 4, and deposits along the free surface $AB$. Fick’s first law states that the interfacial volumetric flux $j$ per unit thickness (in units of m$^2$/s) is related to the gradient of chemical potential $\mu$ (J/m$^3$) by

$$j = D \frac{\partial \mu}{\partial s}$$  \hspace{1cm} (5)

where $s$ is the arc length and $D$ is a temperature dependent interfacial diffusivity (in units of m$^6$/J/s) and is given by the following expression in terms of a reference diffusivity $D_0$, atomic volume $\Omega$, interface thickness $\delta$, thermal activation energy $q$ and Boltzmann constant $k$

$$D = \frac{\delta \Omega}{kT} D_0 \exp\left(-\frac{q}{kT}\right)$$  \hspace{1cm} (6)

Conservation of mass as the material rearranges by diffusion dictates the following relationship between the normal velocity $v_n$ at each point of an evolving interface (either a grain boundary or a free surface) and the flux $j$ (Cocks et al., 1999)

$$v_n + \frac{\partial j}{\partial s} = 0$$  \hspace{1cm} (7)

For the asperity geometry of Fig. 4, with the assumption that $\beta$ is constant and given by Eq. (2), $v_n$ at each point of a grain boundary or free surface can be expressed as a function of the current geometry (i.e. as a function of $u_1$) and is directly proportional to the rate of change of $u_1$ with time, i.e. $\dot{u}_1$.

3.3. Thermodynamic variational principle (TVP)

At a given instant the state of the material can be expressed in terms of $u_1$. In order to complete the constitutive description we need to determine $\dot{u}_1$. We do this by using the variational principle given by Eq. (1), which requires expressing $\Psi$ and $\dot{\mathcal{G}}$ in terms of $\dot{u}_1$. 

3.3.1. Determination of Gibbs free energy

Consider a slice of thickness \( \lambda \) of the repeating cell \( d \times d \) subjected to a stress \( \sigma_{11} \) as shown in Fig. 3. Following Hutchinson et al. (2006) we assume that the elastic properties are constant, i.e. they do not depend on the state of the material. Also, the variational principle described by Cocks et al. (1999) assumes that the body is in a state of mechanical equilibrium. There is then no change in the elastic response as the body sinters at constant stress. For the purpose of developing a model for the sintering response we can treat the body as elastically rigid. The Gibbs free energy then only has contributions from the interface energy and the potential energy of the applied stress and is given by

\[
G_T = G_i + \sigma_{11} d \dot{\varepsilon}
\]

where the reference for the definition of the potential energy of the applied stress is the reference configuration of Fig. 4a. \( G_i \) is the interface energy and is given by Hutchinson et al. (2006)

\[
G_i = d [2b_1 \gamma_g + 2l_1 \gamma_s + (\lambda - 2b_1) \gamma_{11}]
\]

Substituting for \( b_1 \) and \( l_1 \) using Eq. (3) we obtain \( G_i \) as a function of \( u_1 \)

\[
G_i(u_1) = d \left[ \left( \lambda - \sqrt{\lambda^2 - 4\lambda u_1 \cot \beta} \right) \gamma_g + \gamma_s (\sec \beta + 1) \sqrt{\lambda^2 - 4\lambda u_1 \cot \beta} \right]
\]

The Gibbs free energy density \((G)\) is obtained by dividing the Gibbs free energy by the volume of the representative volume element of Fig. 3.

\[
G = \frac{G_i(u_1)}{d^2 \lambda} + \frac{\sigma_{11} d \dot{\varepsilon}}{d^2 \lambda}
\]

Then \( \dot{G} \) is obtained by differentiating Eq. (11) with respect to time:

\[
\dot{G} = \left[ \frac{2\lambda \cot \beta (\gamma_g - \gamma_s \sec \beta \gamma_{11})}{d \sqrt{\lambda^2 - 4\lambda u_1 \cot \beta}} + \frac{\sigma_{11} d}{d} \right] \dot{u}_1
\]

3.3.2. Determination of rate potential

We now introduce the rate potential \( \Psi \) arising from diffusional flow of material over the asperities for the representative volume element of Fig. 3. The potential \( \Psi \) is expressed in terms of the volumetric flux per unit depth \( j \) as given below. This interfacial flux is a function of the local co-ordinate \( s_1 \) along the contact OA, and of the local co-ordinate \( s_2 \) along the free surface AB, as shown in Fig. 4.

\[
\Psi = \frac{d}{D_g} \int_0^{b_1} j^2(s_1) ds_1 + \frac{d}{D_s} \int_0^h j^2(s_2) ds_2
\]

where \( D_g \) and \( D_s \) are the diffusion coefficients for interfacial diffusion along contact OA and surface diffusion along the free surface AB, respectively, as specified by Eq. (6). The resulting flux pattern has been determined by Hutchinson et al. (2006). Using their result, we find that the rate potential per unit volume of TBC is given by

\[
\Psi(u_1) = \frac{\dot{u}_1^2}{24 d^2 D_g \cos \beta} \left[ \lambda - \sqrt{\lambda^2 - 4\lambda u_1 \cot \beta} \right]^2 \left[ \lambda \cos \beta - \left( \cos \beta - \frac{D_g}{D_s} \right) \sqrt{\lambda^2 - 4\lambda u_1 \cot \beta} \right]
\]

which is quadratic in the degree of freedom \( \dot{u}_1 \).

3.3.3. The constitutive model

Substituting \( \dot{G} \) given by Eq. (12) and \( \Psi \) given by Eq. (14) into Eq. (1) and choosing the value of \( \dot{u}_1 \) that minimises the resulting functional gives the rate of evolution of the microstructure as a function of the current state and applied stress. It proves convenient to write the resulting relationships in dimensionless form. All the length scales are normalised by the wavelength of undulation \( \lambda \), such that

\[
\bar{d} = \frac{d}{\lambda}; \quad \bar{u}_1 = \frac{u_1}{\lambda}; \quad \bar{w}_1 = \frac{w_1}{\lambda}; \quad \bar{b}_1 = \frac{b_1}{\lambda}; \quad \bar{l}_1 = \frac{l_1}{\lambda}
\]

and the non-dimensional material properties are

\[
\bar{D}_g = \frac{D_g}{D_s}; \quad \bar{\gamma}_g = \frac{\gamma_g}{\gamma_s}; \quad \bar{E} = \frac{E \lambda}{(1-v)\gamma_s}
\]

with the non-dimensional stress given by

\[
\bar{\sigma}_{11} = \frac{\sigma_{11} \lambda}{(1-v)\gamma_s}
\]
These normalisations are consistent with the normalised time measure

\[ \bar{t} = \frac{D_s \gamma_s \bar{t}^4}{\lambda^4} \]  

Minimisation of the functional gives

\[ \bar{u}_1 = -\frac{\bar{\sigma}_{11} - \bar{\sigma}_1(\bar{u}_1)}{A(\bar{u}_1)} \]  

where

\[ \bar{\sigma}_1(\bar{u}_1) = \frac{2 \cot \beta (1 + \sec \beta - \gamma_s)}{(1 - \nu) \sqrt{1 - 4\bar{u}_1 \cot \beta}} \]

\[ A(\bar{u}_1) = \frac{1}{12(1-\nu)D_s \cos \beta} \left[ 1 - \sqrt{1 - 4\bar{u}_1 \cot \beta} \right]^2 \left[ \cos \beta - (\cos \beta - D_s) \sqrt{1 - 4\bar{u}_1 \cot \beta} \right] \]

\[ \bar{\sigma}_1(\bar{u}_1) \] is the sintering potential associated with sintering of asperities in the \( x_1 \) direction. Note that sintering is arrested when the in-plane stress, \( \bar{\sigma}_{11} \), equals the sintering potential \( \bar{\sigma}_1(\bar{u}_1) \). The strain-rate \( \dot{\varepsilon}_{11} \) can be obtained by differentiating Eq. (4) with respect to time, i.e.

\[ \dot{\varepsilon}_{11} = -\frac{\bar{u}_1}{\bar{t}} \]

Combining Eqs. (19) and (21) gives

\[ \dot{\varepsilon}_{11} = \frac{\bar{\sigma}_{11} - \bar{\sigma}_1(\bar{u}_1)}{A(\bar{u}_1)} \equiv f_{11} \]

Repeating this analysis for a stress \( \sigma_{22} \) applied in the \( x_2 \) direction, we obtain

\[ \dot{\varepsilon}_{22} = \frac{\bar{\sigma}_{22} - \bar{\sigma}_1(\bar{u}_2)}{A(\bar{u}_2)} \equiv f_{22} \]

We assume that \( \dot{\varepsilon}_{13} = \dot{\varepsilon}_{23} = \dot{\varepsilon}_{12} = 0 \). We complete the model by specifying a relationship for the shear strain rate in the 1–2 plane as

\[ \dot{\varepsilon}_{12} = \frac{\bar{\sigma}_{12}}{2\eta} \]

in dimensionless form, where \( \eta \) is the shear viscosity and \( \eta = \eta D_s/(1-\nu)\lambda^3 \).

These equations have been coded into ABAQUS using the UMAT facility. The Newton–Raphson scheme employed to solve the system of equations is detailed in Appendix A. The resulting code has been used to simulate the sintering response of a constrained TBC as detailed in the following sections.

4. Influence of imperfections on the sintering of a constrained TBC

Kumar (2010) has modelled the sintering of a perfect intact coating using the constitutive model of Section 3 and demonstrated that the results are in agreement with those of Hutchinson et al. (2006). It has also been observed through a number of computational simulations that the sintering response of the TBC is not influenced by the choice of Poisson’s ratio, \( \nu \). Here we concentrate on the behaviour of coatings that contain defects. We start by examining the situation where both diffusional processes determine the rate of sintering and take \( D_s = 1 \). From micrographs of EB-PVD coatings, such as those presented by Lughi et al. (2004) we find that the wavelength, \( \lambda \), is in the range 0.2–2 \( \mu \)m and the size of the columnar grains is in the range 2–10 \( \mu \)m. Therefore, \( \overline{\Delta} \) can vary from 1 to 50. Unless otherwise stated, we assume that \( \nu = 0.3, \overline{\Delta} = 20, D_s = 1, \gamma_s = 0.68, \beta = 0.8871 \) and \( \eta = 25 \) in the simulations presented below. It has been observed from the simulations (presented in the subsequent sections) that the value of \( \overline{\Delta} \) influences the sintering response of the coating slightly but it does change the overall failure behaviour.

4.1. Progressive sintering of columns within a mud cracked cluster

Here we explore the inter-columnar sintering of the mud-cracked TBC shown in Fig. 2b. Following Hutchinson et al. (2006) we assume that a fully developed mud cracking pattern has developed. The mud cracked TBC is idealised as an assembly of square clusters of columns as shown in Fig. 2b. We take a single square cluster of side length \( 2R \) and height \( H \),
which is perfectly bonded to the underlying substrate. The FE model is fixed at the bottom in all three directions and all other faces are traction free. The FE model is constructed with C3D8 8-noded linear brick element. An initial condition of $\pi'_1 = \pi'_2 = 0.05$ is taken for all the elements. The FE analysis shows that full sintering occurs (i.e. $\beta_1 = \beta_2 = 0.5$) within the square cluster for small values of $E$. Fig. 5 shows the semi-contact width $\beta_2$ in the $x_2$ direction at a time $t = 7.8 \times 10^{-4}$ for $E = 1500$ and $R/H = 0.5$. It is evident that sintering is non-uniform in the cluster. In their analytical model, Hutchinson et al. (2006) assumed that the sintering strains, i.e. $\beta_1, \beta_2$, are uniform in the cluster. With this assumption they demonstrate that the sintering response of the cluster can be determined by the analytical expressions for a perfect fully constrained layer, but using a modified value of Young’s modulus. Following the procedure adopted by Hutchinson et al. (2006) for determining the elastic stored energy per unit volume of a cluster, we find that for the square profile considered here that

$$U_{sq} = \frac{4}{3\sqrt{6}} E \left(\frac{R}{H}\right) (\varepsilon^t + \varepsilon^T)^2$$

for $\nu = 0.5$ and $H > R/\sqrt{6}$, where $\varepsilon^t$ and $\varepsilon^T$ are the in-plane sintering and thermal mismatch strains in the coating. The strain energy density in a perfect constrained film is

$$U_{pf} = \frac{E_{eff}}{(1-\nu)} (\varepsilon^t + \varepsilon^T)^2$$

Equating Eqs. (25) and (26), and taking $\nu = 1/2$ for an elastically incompressible film, we find the effective modulus ($E_{eff}$) of a perfect film equivalent to a mud cracked island cluster to be

$$E_{eff} = \frac{2}{3\sqrt{6}} E \left(\frac{R}{H}\right)$$

Fig. 6 shows the evolution of the average value of $\beta_2$ within the cluster compared with the prediction for a perfect film using the modified modulus of Eq. (27). It is evident from Fig. 6 that the simplified model provides an accurate description of the overall sintering response, both in terms of timescale for the sintering process and the overall extent of the sintering behaviour. Also, it is evident that for the value of $R/H$ used in these simulations the constraint from the substrate is experienced over a height $H/4$, within which there is significant shear deformation (evidenced by the exaggerated distorted shape of the mesh in Fig. 5). Above this height sintering is reasonably uniform within the cluster. Both these observations are consistent with the assumptions made in the model of Hutchinson et al. (2006). We make use of these observations in Section 5, where we use similar approximations to model the growth of imperfections in the coating.

4.2. Influence of a square array of imperfections

We now consider a square array of imperfections within the constrained TBC and study the influence of these imperfections on the sintering response. Within the imperfection an initial condition which differs from that in the remainder of the coating is specified. All other geometric and material parameters are kept the same. Kumar (2010) has evaluated a range of problems of this type and has demonstrated that for situations where a perfect coating can fully densify (i.e. a compliant coating) the response is not sensitive to the presence of small variations in the initial conditions and the entire coating fully densifies. A completely different type of behaviour is observed for stiff coatings. A FE model of a representative material volume similar to that shown in Fig. 5 was employed. Symmetry conditions are imposed at all boundaries perpendicular to the $x_1$ and $x_2$ directions. The initial condition ($\pi'_1 = \pi'_2 = 0.07$) for the defective elements within a cluster of elements which extends down the entire height ($x_3$-direction) of the TBC is slightly less than that in the remainder of the coating ($\pi'_1 = \pi'_2 = 0.08$). For $E = 1000$, the FE analysis indicates that the imperfection and surrounding
material densify initially at a rate similar to that for the perfect film. As the in-plane tensile stress builds up due to generation of elastic strain to balance the sintering strain, the rate of sintering slows. As sintering is about to arrest, as in the case of the perfect coating, we observe a divergence in the response at the imperfection compared with the remainder of the coating. This is illustrated in Fig. 7 which shows the evolution of \( b_2 \) within the imperfection and surrounding material, compared with that for the perfect coating. Desintering occurs at the location of the initial imperfection, i.e. \( b_2 \) decreases for \( t > 1.2 \times 10^{-3} \). As it does so, the constraint on the remaining material is relaxed allowing the surrounding material to sinter faster. Eventually, \( b_2 = 0 \) at the site of the imperfection. This occurs initially at the surface of the TBC. The desintered zone then spreads vertically towards the substrate and horizontally towards the axis of symmetry, where it meets with an equivalent spreading desintered zone from the adjacent imperfection to form a band of desintered material.

Fig. 6. Evolution of semi-contact width \( b_2 \) in \( x_2 \) direction of analytical model is compared with average semi-contact width \( \overline{b}_2 \) of finite element model for \( E = 1500 \) and \( R/H = 1/2 \).

Fig. 7. Evolution of semi-contact width \( \langle b_2 \rangle \) at the imperfection and away from imperfection compared with perfect film for \( E = 1000 \).
This localised desintering reduces the constraint on the surrounding material allowing it to sinter faster. Fig. 8 shows the semi-contact width ($b_2$) in the $x_2$-direction following the spread of the desintering region from the initial imperfection (i.e. at $T = 4 \times 10^{-3}$), which is the set of highlighted elements in the centre of the repeating cell. A negative value of $b_2$ is a measure of separation between the columns of the TBC. For this value of $E$ the constraint on elements away from the defect is not relaxed sufficiently to allow them to reach full density and sintering is arrested when $b_2 = 0.2461$. A similar pattern of cracks is observed when imperfections are only introduced in elements adjacent to the top surface of the coating.

4.3. Influence of a family of imperfections

The analysis of the previous sub-section indicates that in compliant systems the sintering response is not sensitive to the presence of small imperfections, but if the system is stiff small imperfections can eventually develop into cracks, which propagate through the coating. We explore this further by examining the sintering response when the coating contains a regular pattern of interconnected imperfections. Fig. 9 shows the idealised TBC structure with a primary set of imperfections running along the boundaries of the cluster. These imperfections are assigned a slightly different contact condition than within the cluster. We consider a repeating cluster of size $2R \times 2R$ which has a primary imperfection on its boundary. The imperfection exists over the entire height ($x_3$-direction) of the TBC. In the simulations presented here $R = H$. The FE model of this cluster consists of 3800 C3D8 uniform 8 noded brick elements. The FE model is fixed at its base in all three directions and constrained around the vertical boundaries. The initial condition of defect free elements is $u_0^i = 0.05$, $u_0^2 = 0.05$. Along the imperfection, $u_0^i = 0.045$ for the direction perpendicular to the line of imperfection and $u_0^i = 0.05$ parallel to the imperfection. Here, $i$, ranges over 1, 2. For small values of $E$ the response is not sensitive to the imperfections and the entire coating fully sinters. For values of $E > 600$ desintering occurs at the imperfections which develop into cracks. This reduces the constraint on the surrounding material allowing it to sinter faster and to a greater extent than that experienced in a perfect coating. For large values of $E$ sintering within the cluster is eventually arrested and the terminal state is almost exactly the same as that for the isolated cluster considered in Section 4.1. Also note that the pattern of cracks in the terminal state is the same as that resulting from the initial pattern of imperfections considered.
in Section 4.2. Thus the pattern of cracks is insensitive to the detailed form of the imperfections and only depends on their spacing. Similar crack patterns are observed for coatings comprising imperfections only in the elements at the top surface of the coating. We postpone a more detailed discussion of these simulations until the next section where we develop a simple 2 degree of freedom model of this problem.

5. Evolution of a family of imperfections in a two state variable system

The above simulations provide insight into situations where mud cracking might occur in practice, but in order to map out the role of the different geometric and material parameters it would be necessary to undertake a wide range of computer simulations. The ability of the simplified model developed by Hutchinson et al. (2006) in simulating the response of an isolated cluster as described in Section 4.1 motivates us to develop a model with a similar degree of complexity for the growth of imperfections. The simulations presented in the last section will allow us to assess the validity of any assumptions made in the model.

In this section we develop a two state variable Rayleigh-Ritz type model. We concentrate on the geometric problem analysed in Section 4.3. A representative repeating element is chosen that has primary imperfections within it as shown in Fig. 9. In the computational studies the imperfection extended throughout a continuum element. Within the model developed in this section we assume that the defect exists along a single line of contacts between adjacent columns. This is a more realistic assumption.

For completeness we include the effect of thermal strains in the following analysis, although in the calculations presented here we limit our consideration to situations in which the thermal strains are zero at the sintering temperature. Isothermal conditions are imposed within the repeating cluster which may be greater than or less than the deposition temperature \( T_{D} \). The thermal expansion mismatch strain is uniform in the plane of the coating, such that \( e_{11}^{T} = e_{22}^{T} = e^{T} \), with \( e^{T} \) given by

\[
e^{T} = \frac{\alpha_{c}(T-T_{D}) - \alpha_{s}(T-T_{D})}{C_{0}} \tag{28}
\]

where, \( \alpha_{c} \) and \( \alpha_{s} \) are the coefficients of thermal expansion of the TBC and substrate, respectively. The deposition temperature \( T_{D} \) is taken as the reference temperature and defines the initial stress-free condition of the TBC. The objective is to determine the time evolution of the sintering of clusters and primary imperfections and to determine under what condition a fully developed crack forms due to the imposed thermal mismatch associated with the change in temperature from the deposition temperature.

As inter-columnar sintering proceeds, a biaxial sintering strain \( e_{ij}^{s} \) evolves with time, with \( e_{11}^{s}, e_{22}^{s} \) the only non-zero values of sintering strain. Following Hutchinson et al. (2006) we assume that the sintering strain is uniform within the cluster and that \( e_{11}^{s} = e_{22}^{s} = e^{s} \). \( e_{ij}^{s} \) can then be conveniently split into two fields, one analogous to progressive sintering of columns in a perfect constrained TBC film with sintering strain \( e_{ij}^{s1} = e^{s1} \delta_{ij} \) where \( \alpha \) and \( \beta \) can have values over the range 1, 2, and the other corresponding to inter-columnar sintering of an isolated cluster with sintering strain \( e_{ij}^{s2} = e^{s2} \delta_{ij} \) as shown in Fig. 10, where

\[
e^{s} = e^{s1} + e^{s2} \tag{29}
\]

The substrate is taken to be much thicker than the TBC layer, such that the in-plane strain in the TBC layer relative to the substrate is zero. Consequently, the elastic strain \( e_{ij}^{e1} \) in field 1 of the cluster is uniform as illustrated in Fig. 11a and is given by

\[
e_{ij}^{e1} = -(e_{ij}^{s1} + e_{ij}^{s2}) \tag{30}
\]

In field 2 of the cluster, we assume that the deformation is constrained up to height \( \xi \) in the \( x_{3} \) direction measured from the substrate (see Fig. 11b). The following compatibility condition needs to be satisfied in field 2:

\[
(e_{11}^{s2}(x_{3}) + e_{22}^{s2})2r - \Delta u'(x_{3}) = 0 \tag{31}
\]

![Fig. 10. Decomposition of fields in a square cluster with primary imperfections (P.I). Field 1: analogous to progressive sintering of columns in a perfect constrained TBC film with sintering strain \( e^{s1} \) and thermal mismatch strain \( e^{T} \) and Field 2: corresponding to inter-columnar sintering of an isolated cluster with sintering strain \( e^{s2} \).](image-url)
Here, $\Delta u(x_3)$ is the net displacement across the primary imperfection, i.e. between the columns either side of the imperfection. An equivalent relationship holds for the $x_2$ direction. An elastic field exists and varies in the bottom portion of the cluster. The elastic constraint of the substrate alters the local contact condition along the primary imperfection. Similar to the analysis of Section 3, the thermodynamic variational principle is employed to calculate the time evolution of $\varepsilon^1$ and $\varepsilon^2$ based upon the assumed contact geometry shown in Fig. 4 between neighbouring TBC columns within a cluster and at the primary imperfections. We assign subscripts 'cl' and 'cr' to characterise the geometric parameters within the cluster and imperfections, respectively. We again assume an equilibrium asperity profile angle $\beta$ for the contact geometries in both the imperfection and cluster. We can then express all variables along the imperfection as a function of $u_{cr}$ and those in the cluster as a function of $u_{cl}$.

5.1. Geometric coupling between local and global scales

The macroscopic sintering strains $\varepsilon^1$ in field 1 and $\varepsilon^2$ in field 2 can be expressed in terms of the state variables and their respective initial values. The elastic field associated with field 2 gives the net displacement across the primary imperfection

$$\Delta u(x_3) = \begin{cases} 2R\varepsilon^2 \xi & \text{if } 0 \leq x_3 \leq \xi; \\ 2R\varepsilon^2 & \text{if } \xi \leq x_3 \leq H. \end{cases}$$

(32)

The primary unknown at the contacts within the cluster $u_{cl}$ can be expressed as

$$u_{cl} = u_{0}^{cl} - (\varepsilon^1 + \varepsilon^2)d$$

(33)

The local approach at the primary imperfection is given by

$$u_{cr}(x_3) = u_{cr}^{0} - (\varepsilon^1 + \varepsilon^2)d + \Delta u(x_3)$$

(34)

where $u_{0}^{cl}$ and $u_{0}^{cr}$ are the initial values of the kinematic variables $u_{cl}$ and $u_{cr}$, respectively.

Note that $u_{cr}(x_3) = u_{cr}$ at $x_3 = \xi$. Here $u_{cr}$ is the state variable at the imperfection. Manipulating the expressions for $u_{cr}$ and $u_{cl}$ given above, we can express the sintering strains in the two fields as functions of the two state variables $(u_{cr}, u_{cl})$ as follows:

$$\varepsilon^1 = \frac{u_{cl}^{0} - u_{cl}}{d} - \left(\frac{(u_{cr} - u_{cr}^{0}) - (u_{cl} - u_{cl}^{0})}{2R}\right)$$

(35)

and

$$\varepsilon^2 = \left(\frac{(u_{cr} - u_{cr}^{0}) - (u_{cl} - u_{cl}^{0})}{2R}\right)$$

(36)

The elastic strains and elastic stored energy can be expressed in terms of $u_{cr}$ and $u_{cl}$ by combining Eqs. (30), (31), (35) and (36). The rate of change of Gibbs free energy $G$ and rate potential $\Psi$ can be expressed in terms of $u_{cr}$ and $u_{cl}$ by making use of the relationships in Section 3 applied to each type of contact. The thermodynamic variational principle of Eq. (1) can then be used to determine the rate of evolution of the microstructure in terms of $(u_{cr}, u_{cl})$. The minimisation process
provides two linear simultaneous equations for the rates

\[
\begin{bmatrix}
\frac{\partial^2 \psi}{\partial u_{cr}^2} & \frac{\partial^2 \psi}{\partial u_{cr} \partial u_{cl}} \\
\frac{\partial^2 \psi}{\partial u_{cr} \partial u_{cl}} & \frac{\partial^2 \psi}{\partial u_{cl}^2}
\end{bmatrix}
\begin{bmatrix}
\dot{u}_{cr} \\
\dot{u}_{cl}
\end{bmatrix} = - \begin{bmatrix}
\frac{\partial C}{\partial u_{cr}} \\
\frac{\partial C}{\partial u_{cl}}
\end{bmatrix}
\]

(37)

This matrix can be inverted algebraically to obtain \((u_{cr}, u_{cl})\) as a function of the current state \((u_{cr}, u_{cl})\). The time evolution of \((u_{cr}, u_{cl})\) follows by time integration of a set of nonlinear ODEs using a fourth-order Runge–Kutta (R–K4) method.

Detailed relationships for the quantities in Eq. (37) are given in Appendix B. When solving the system of equations it again proves convenient to express the equations in dimensionless form. As before we employ the normalisations of (15)–(18). In addition, we define the following normalised geometric parameters:

\[
x_3 = \frac{x_3}{l}; \quad \Pi = \frac{H}{l}; \quad \tilde{R} = \frac{R}{H}
\]

(38)

5.2. Predictions of the two state variable analytical model

The system of nonlinear ODEs are solved with initial contact conditions \(u_{cr}^0 = u_{cl}^0 = 0.045\) and \(u_{cl}^0 = 0.05\). Other geometric and material parameters are the same as those used in the computational study of Section 4. Four different types of behaviour are observed depending upon the magnitude of \(E\) and the size of the cluster \(\tilde{R}\) as shown in Fig. 12. As before, for low values of \(E\), complete sintering occurs both in the cluster and at the primary imperfections regardless of the cluster size, and the sintering response is the same as that for a perfect coating. For moderate values of \(E\), elastic constraint of the TBC layer is just sufficient to switch off sintering at the primary imperfections, while full sintering occurs in the cluster. This is true for any cluster size \(\tilde{R}\). In contrast, when \(E\) is large, significant tensile stresses develop in the TBC which almost arrest sintering. The constraint is then relieved by desintering at the imperfections and by the development of cracks along the lines of the imperfections. This localised desintering phenomenon can be understood by examining how the sintering potential, \(\sigma_s\), and in-plane stress evolve. The sintering potential is a monotonically increasing function of \(\Pi\) and hence the in-plane (compressive) sintering strain. The in-plane stress is determined by the sintering response in the cluster. As the coating sinters the in-plane stress and sintering potential in the cluster increase, but the difference between them gradually decreases until they become equal to each other and sintering is eventually arrested. The stress across the imperfection is the same as that experienced in the cluster, but the sintering potential is always less than that in the cluster and therefore the rate of sintering is slower. As the in-plane stress approaches the sintering potential in the cluster, it eventually exceeds the sintering potential across the imperfection. This results in desintering along the line of imperfection. This also results in a decrease in stress across the imperfection, but the sintering potential reduces at a faster rate, thus the columns continue to separate locally until a crack forms. During this process the stress is also relieved within the cluster to a value less than the sintering potential allowing it to sinter further.

Complete sintering occurs in the clusters if the spacing of the imperfections \(\tilde{R}\) is relatively small. The evolution of the half contact width, \(\delta\) for the cluster and imperfection are shown in Fig. 13a for \(E = 700\) and \(\tilde{R} = 1\) and compared with the FE results of Section 4.3. The displacement field that we assume for the imperfection, Eq. (32), varies linearly up to a height \(\zeta\),
and then is constant with increasing height. This results in a variation of the half contact width along the height of the imperfection. In this and subsequent figures the value of $b$ in the uniform top section of the coating is plotted. We obtain the solution in terms of the primary unknowns $(u_{cr}, u_{cl})$. A negative value of $u_{cr}$ indicates physical separation of an interface at the imperfection. However, we plot the graphs here in terms of $(b_{cr}, b_{cl})$ for the sake of convenience. It should be noted that when the semi-contact width, $b_{cr} \rightarrow 0$, a fully developed crack forms at the interface. Physically, $b_{cr}$ cannot be less than zero and a negative value of $b_{cr}$ simply indicates physical separation at the top portion of an imperfection. It can be seen that the analytical model captures the essential physics, with the timescales for the development of the imperfections and form of behaviour being comparable with the FE simulation. The differences arise in part from the approximations employed in the analytical model, but it should also be noted that the imperfections are treated in a different way in the two situations. In the analytical model the imperfection is a line defect, while in the computations the defect has a width equal to the element size.

Increasing $\tilde{R}$ increases the constraint on the sintering process and prevents full sintering being achieved in the cluster. This is shown in Fig. 13b for $\tilde{R} = 2$ and $E = 1000$. Again, the analytical results agree closely with the FE results. From a series of simulations of this type we can determine how different characteristics of the sintering behaviour depend on the geometric and material parameters. A full evaluation is provided by Kumar (2010). Fig. 14 shows how the time for the
initiation of desintering at the imperfections depends on the cluster size, $R$ for $E = 1500$ and $H = 200$. This reflects a general trend with instabilities occurring initially at the most widely spaced imperfections.

The results presented here are not very sensitive to the choice of the values of $u_{0}^{cl}$ and $u_{0}^{cr}$ provided that they are small compared to the major dimensions of the asperities and that $u_{0}^{cr}$ is less than $u_{0}^{cl}$. Increasing $u_{0}^{cl}$ decreases the sintering strain at which sintering is arrested in a perfect film, but increases the magnitude of the in-plane stress. For the two state variable problem, increasing $u_{0}^{cl}$ leads to a reduction in the time at which sintering is arrested in the cluster and desintering is initiated at the site of an imperfection, while a reduction in the difference between $u_{0}^{cl}$ and $u_{0}^{cr}$ results in an increase of this time. These effects are small compared to the overall time required for coating to sinter, but when evaluating trends in the predicted response it is important to employ the same values of $u_{0}^{cl}$ and $u_{0}^{cr}$ in the simulations.

The simulations presented here allow the conditions under which mud cracks will develop in a coating to be identified, but they do not provide any information about the mud crack pattern. In order to do this we need to consider the response of a body which contains a number of different types of imperfections. This is the subject of the next section.

6. Evolution of two families of imperfections in a three state variable system

In the problem of Section 5 we have modelled the development of a primary set of imperfections in the TBC layer during progressive sintering. The analysis identifies the conditions under which mud cracks can form, but it does not provide any information about the final pattern of cracks in the coating. The analysis suggests that the wider the spacing of the imperfections the faster they develop into cracks, see Fig. 14. This suggests that the initial cracks that form will be widely spaced. We might, however, expect imperfections at intermediate positions to subsequently develop into cracks, with this process repeated until the crack density saturates. The question now is “what is the final steady state spacing of the cracks?”. In order to answer this, we formulate another problem in which we follow the evolution of two families of imperfections. The primary imperfections form a square grid of spacing $2R$ as before. Supersimposed on top of this is a square grid of secondary imperfections, also of spacing $2R$, whose lines bisect the sides of the grid of primary imperfections as shown in Fig. 15. We can identify a representative square cell of side $2R$, with secondary imperfections forming the boundary of the cell and primary imperfections bisecting the cell to form four equal square sub-cells of size $R$.

We can analyse this problem in a similar way to the problem of Section 5. The sintering strain $e_{ij}$ can now be decomposed into three fields

$$e = e^{1} + e^{2} + e^{3} \tag{39}$$

Field 1 is the same as that for inter-columnar sintering of columns in a perfect constrained TBC film with sintering strain $e^{1}$ and thermal mismatch strain $e^{T}$. Field 2 is similar to that for the sintering of columns of an isolated cluster as described in Section 4.1, with sintering strain $e^{2}$. Field 3 is similar in form to Field 2, but is associated with each sub-cluster. The detailed form of these fields is given in Appendix C. The subscripts ‘cr’, ‘cl’ and ‘cr2’ are used to characterize the geometric parameters at the primary imperfections, bulk contacts in the cluster and secondary imperfections respectively. The compatibility conditions given by Eqs. (30) and (31) are still valid for fields 1 and 2, respectively. The following
additional compatibility condition for field 3 needs to be satisfied in each sub-cluster:

\[ (e_1^3(x_3) + e_2^3(x_3)) R - \Delta u_{cr2}(x_3) = 0 \] (40)

Here, \( \Delta u_{cr2}(x_3) \) is the net displacement across the secondary imperfection. As before, we assume an equilibrium asperity profile angle \( \beta \). The entire response can now be expressed in terms of the evolution of three degrees of freedom \( (u_{cr}, u_{cl1}, u_{cr2}) \). The sintering and elastic strains associated with the three fields can be expressed in terms of material parameters, including the initial values of \( u_{cr} \), \( u_{cl1} \), and \( u_{cr2} \).

This set of nonlinear ODEs was solved numerically to obtain time evolution of \( (u_{cr}, u_{cl1}, u_{cr2}) \) using a fourth order Runge-Kutta (R–K4) integration scheme.

6.1. Predictions of analytical model

If \( \mathcal{E} \ll 600 \) complete sintering of the cluster and imperfections occurs independent of the choice of geometric and other material parameters, including the initial values of \( u \) in the cluster and along the two families of imperfections. For larger values of \( \mathcal{E} \) we observe two major different types of mud cracking behaviour, depending on the magnitude of \( \mathcal{E} \) and the size of the cluster \( \mathcal{R} \). Consider, by way of illustration, the situation where \( \mathcal{E}_{cr} = 0.045 \), \( \mathcal{E}_{cl1} = 0.055 \) and \( \mathcal{E}_{cr2} = 0.05 \). For \( \mathcal{E} = 3000 \) and \( \mathcal{R} = 1.2 \), cracks fully develop at the primary imperfections, while the secondary imperfections fully densify, and sintering is arrested in the cluster before full density is achieved as shown in Fig. 16a. Full sintering of the secondary imperfections appears counter intuitive. One might expect sintering to be arrested in a similar way to that observed in the cluster. It is interesting to note, however, that for situations where an initial imperfection is introduced into a coating such that \( \mathcal{E}_{cr} > \mathcal{E}_{cl1} \) full densification can occur at the site of the imperfection, while the cluster only partially sinters. This illustrates that depending on the magnitude of the imperfection we can either get cracking or localised densification. In the context of Fig. 16a, this suggests that it is not energetically favourable for a secondary crack to form, but it is possible for local densification to occur, promoted by small differences in the sintering response at these locations with increasing time. We explore this behaviour more fully in the next sub-section, where we examine the computational results for the growth of secondary cracks.

Increasing \( \mathcal{R} \) to 1.4, the primary and secondary imperfections develop into cracks as shown in Fig. 16b. As before the cluster does not fully densify, but formation of the secondary cracks reduces the constraint on the sintering process and a higher density is achieved than for the situation \( \mathcal{R} = 1.2 \) shown in Fig. 16a. From a series of simulations of this type, where we systematically change \( \mathcal{E} \) and \( \mathcal{R} \), we can map out the conditions under which the different types of behaviour typified by Fig. 16a and b occur. The resulting map is shown in Fig. 17. As \( \mathcal{E} \) is increased the value of \( \mathcal{R} \) at the transition between the two types of behaviour (i.e. the limiting crack spacing) increases. This reflects the fact that the larger the value of \( \mathcal{E} \), the greater the constraint on sintering, which results in a smaller build-up of elastic strain energy in the coating to drive the desintering and cracking process. These calculations correspond to an idealised geometric situation, but Fig. 17 suggests that once the crack spacing has reduced to that represented by the solid line on the figure, no further cracking can occur. Thus the line provides an indication of the value of \( \mathcal{R} \) at which saturation of cracks occurs. Consider the case where \( \mathcal{E} = 3000 \). Fig. 17 then gives the transition between the two cracking patterns at \( \mathcal{R} \approx 1.3 \). Thus for a primary spacing of the imperfections slightly less than this value cracks will form only at the primary imperfections with a spacing 2\( \mathcal{R} \), while for
A slightly larger value of \( \tilde{R} \) cracks will form at both the secondary and primary imperfections giving a crack spacing \( \tilde{R} \). For a coating with this normalised modulus we would therefore expect to see a pattern of cracks with spacing, \( CS \), in the range \( 1.3H \leq CS \leq 2.6H \), where \( H \) is the thickness of the coating, with the spacing increasing with increasing stiffness of the coating. Young’s modulus of the ceramic coating measured by in-situ experiments is in the range 5–40 GPa. From the micrographs of the EB-PVD coatings it can be seen that the wavelength \( \lambda \) ranges from 0.2–2 \( \mu \)m. These values correspond to a non-dimensional modulus range \( E = 1500–120000 \). We explored the sintering response of the EB-PVD in this study for a coating modulus in the range \( E = 300–7000 \). The system of equations become very stiff at larger values of \( E \) and as \( E \) is increased the amount of sintering strain accumulated in the coating up to the point that the sintering process becomes unstable decreases. Thus extremely small time steps are required to simulate the response, with the results becoming sensitive to numerical noise. The simulations presented here, however, clearly illustrate the physics of the cracking process. Also the mean spacing of the cracks has almost plateaued at the larger values of \( E \) used in the simulations. Over the range of modulus studied the predicted saturated mud-crack spacing, \( CS \), is in the range \( 0.5H \leq CS \leq 3.6H \). Lughi et al. (2004) conducted isothermal and thermal cycling experiments on a 10 \( \mu \)m thickness coating and observed, \( CS \), in the range 30 \( \mu \)m \( \leq CS \leq 100 \) \( \mu \)m. This corresponds to \( 3H \leq CS \leq 10H \). The crack spacing predicted in this study is consistent in the lower range of experimentally observed crack spacing shown in Fig. 2a (Lughi et al., 2004).

Fig. 16. (a) A typical plot showing the formation of primary set of cracks. (b) Formation of primary and secondary set of cracks.
6.2. Computational model

In order to validate the three state variable analytical model a number of computational studies have been undertaken. Here, we consider the situation where there is a fully developed primary set of cracks in the TBC and examine whether a secondary set of imperfections develop into cracks. We consider the situations where $E = 3000$ and $\tilde{R} = 1$ or $2$. These two situations are labelled in Fig. 17 and lie either side of the boundary between the two types of cracking patterns, with the analytical model of Section 6.1 indicating that the secondary imperfections should not develop into cracks when $\tilde{R} = 1$, but secondary cracking is expected when $\tilde{R} = 2$. In these simulations an initial imperfection exists over the entire height ($x_3$-direction) of the TBC. We use the same initial conditions as for the three state variable analytical model. In the defect free elements the initial condition is $u_0^1 = 0.055$, $u_0^2 = 0.055$. For the elements with imperfections the initial condition is $u_0^i = 0.05$, for contacts parallel to the line of the defect and $u_0^i = 0.055$ perpendicular to the defect.

First consider the case with $E = 3000$ and $\tilde{R} = 1$. Contours of constant $b_2$ are shown in Fig. 18a after a time $t = 7.8 \times 10^7$, after which no further sintering occurs. Towards the top of the coating, the columns have fully sintered throughout the cluster and across the initial imperfections. In this region the cluster does not experience any constraint from the coating (as predicted by the Rayleigh Ritz analysis of Section 4.1 for an isolated cluster). Towards the bottom of the coating sintering within the cluster is incomplete and desintering occurs along the imperfections leading to a crack which grows to a quarter of the height of the column. The three state variable model above predicts, Fig. 18a, incomplete sintering within the cluster and complete sintering at the imperfection. As noted in Section 5.2, Fig. 18a gives the value of $b_2$ for $x_3 > \zeta = R/\sqrt{6}$ for the imperfection. It is smaller than this below this height and is the same as that for the cluster adjacent to the substrate. Thus the analytical model correctly predicts complete sintering towards the top of the cluster. It also correctly predicts incomplete sintering towards the substrate, but the simple form of displacement pattern assumed in the model is unable to capture the formation of a crack immediately above the substrate. The terminal state for the situation where $\tilde{R} = 2$ is shown in Fig. 18b. A crack now forms at the secondary imperfection and propagates through the height of the coating. This is consistent with the simplified model of Fig. 16b. Thus the simple three state variable analysis correctly identifies when a secondary crack can grow through the thickness of the coating.

7. Conclusion

In this paper we have presented two complementary approaches for determining the sintering response of an EB-PVD columnar thermal barrier coating and for identifying the conditions under which instabilities can develop in the sintering process, leading to the formation of cracks. A simple constitutive model is developed which has been used in conventional finite element studies to model the sintering response and assess the sensitivity of the response to the presence of imperfections in the coating. Using the same basic material description, two simple models have been developed which express the entire response in terms of only two or three state variables. The predictions of these simpler models have been validated against the full finite element simulations. An advantage of the simple models is that a wide range of geometric conditions with different material properties can be analysed efficiently.

Mud-cracks can form in a coating under conditions where sintering in a perfect coating would be arrested before full density is achieved. As sintering is arrested, desintering can occur at the site of small imperfections within the coating, relaxing the
constraint on the remaining material allowing it to sinter towards a lower energy state. It is demonstrated in Sections 4 and 5 that two conditions need to be satisfied for mud-cracks to form in EB-PVD thermal barrier coatings: the in-plane modulus must be greater than a critical value; and the sintering potential in the constitutive model of Eqs. (22) and (23) must be a monotonically increasing function of the state variable $u_i$, or equivalently, the sintering strain, $\varepsilon$. The in-plane modulus of all practical coatings significantly exceeds the critical modulus and the expression for the sintering potential determined from the model of Section 4 satisfies the condition that it should increase monotonically, see the first of Eqs. (20). Thus we would expect mud cracks to form in practical coating systems under conditions where sintering of the top coat can occur.

A coating can contain a large number of imperfections of different intensity, with cracks forming at different locations at different times during the sintering process. Eventually, the density of cracks will saturate. In Section 6 an assessment of the final crack density has been made using a three degree of freedom model, which follows the evolution of a body which contains two families of imperfections. The transition from one family of imperfections developing into cracks to both families cracking is used to estimate the final density of mud cracks in a coating. The density depends on the in-plane stiffness, with the average spacing increasing with increasing stiffness of the coating. The model presented in Section 6 predicts a crack spacing in the range $0.5–3.6$ times the thickness of the coating. This is at the lower end of the spacing observed by Lughi et al. (2004), who observed crack spacing in the range $3–10$ times the coating thickness.

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Appendix A. Integration scheme for constitutive model

Here we describe the integration scheme used in the computational studies, which is based on a procedure described by Benallal et al. (1988). The constitutive relationships of Eqs. (22), (23) and (24) can be written in incremental form as follows:

\[ F_{ij} = \Delta e_{ij}^e - \Delta T f_{ij}(\sigma_{ij} + \theta \Delta \sigma_{ij} + \theta \Delta e_{ij}^p) = 0; \quad 0 < \theta \leq 1 \]  
(A1)

where \( \Delta e_{ij}^e \) is the increment of sintering strain over the time increment \( \Delta t \), with the rates determined at the instant \( \theta \Delta t \) in the increment. In the simulations presented here a value of \( \theta=0.5 \) was chosen to ensure that the solution is unconditionally stable. The stress and strain increments must satisfy the elastic constitutive law

\[ \Pi_{ij} = \Delta \sigma_{ij} - \Delta f_{ijkl}(\Delta e_{ij} - \Delta e_{kl}^0) = 0 \]  
(A2)

Here we assume that the elastic stiffness matrix \( \Delta f_{ijkl} \) is not a function of state (i.e. sintering strain). Eqs. (A1) and (A2) represent a set of nonlinear equations in unknowns \( (\Delta e_{ij}^p \text{ and } \Delta \sigma_{ij}) \). This system of equations can be solved using Newton’s method. After \( i \) iterations within the increment the values of \( (\Delta e_{ij}^p \text{ and } \Delta \sigma_{ij}) \) are given by

\[ \begin{bmatrix} \Delta e_{ij}^p \\ \Delta \sigma_{kl} \end{bmatrix} = \left[ \begin{bmatrix} \Delta e_{ij}^p \\ \Delta \sigma_{kl} \end{bmatrix} ight]^{i-1} - \left\{ \begin{bmatrix} \delta_{ik} \delta_{jl} - \Delta T \frac{f_{ik} f_{jl}}{\sigma_{kl}} \\ \frac{1}{\Delta t} \delta_{ik} \delta_{jl} \end{bmatrix} \right\}^{-1} \begin{bmatrix} F_{ij} \\ \Pi_{ij} \end{bmatrix} \]  
(A3)

where the superscript \( i-1 \) indicates that all functions are determined using quantities determined at the end of the \( (i-1) \)th iteration. The iterative process is continued until a prescribed tolerance in \( \Delta e_{ij}^p \text{ and } \Delta \sigma_{kl} \) is reached. Explicit forms of Eqs. (A1) and (A2) are given below

\[ F_{11} = \Delta e_{11} - \Delta T f_{11}(\sigma_{11} + \theta \Delta \sigma_{11} + \theta \Delta e_{11}) = 0 \]  
(A4)

\[ F_{22} = \Delta e_{22} - \Delta T f_{22}(\sigma_{22} + \theta \Delta \sigma_{22} + \theta \Delta e_{22}) = 0 \]  
(A5)

\[ \Pi_{11} = \Delta \sigma_{11} - \frac{E}{(1+\nu)(1-2\nu)}[(1-\nu)(\Delta e_{11} - \Delta e_{11}^0) + \nu(\Delta e_{22} - \Delta e_{22}^0) + \nu(\Delta e_{33})] = 0 \]  
(A6)

\[ \Pi_{22} = \Delta \sigma_{22} - \frac{E}{(1+\nu)(1-2\nu)}[\nu(\Delta e_{11} - \Delta e_{11}^0) + (1-\nu)(\Delta e_{22} - \Delta e_{22}^0) + \nu(\Delta e_{33})] = 0 \]  
(A7)

\[ \Pi_{33} = \Delta \sigma_{33} - \frac{E}{(1+\nu)(1-2\nu)}[\nu(\Delta e_{11} - \Delta e_{11}^0) + \nu(\Delta e_{22} - \Delta e_{22}^0) + (1-\nu)(\Delta e_{33})] = 0 \]  
(A8)

\[ F_{33} = \Delta e_{12} - \frac{\Delta T}{2\eta} (\sigma_{12} + \theta \Delta \sigma_{12}) = 0 \]  
(A9)

\[ \Pi_{44} = \Delta \sigma_{12} - \frac{E}{(1+\nu)}[\Delta e_{12} - \Delta e_{12}^0] = 0 \]  
(A10)

\[ \Pi_{55} = \Delta \sigma_{13} - \frac{E}{(1+\nu)}[\Delta e_{13}] = 0 \]  
(A11)

\[ \Pi_{66} = \Delta \sigma_{23} - \frac{E}{(1+\nu)}[\Delta e_{23}] = 0 \]  
(A12)

The above integration scheme has been coded as a UMAT routine in ABAQUS. ABAQUS also requires specification of the Jacobian for use in the solution for the next increment. This can be determined using a procedure originally proposed by Benallal et al. (1988) as described below.

A.1. Determination of Jacobian

The Jacobian is defined as

\[ J_{ijkl} = \frac{\partial \Delta \sigma_{ij}}{\partial \Delta e_{kl}} \]  
(A13)
Note that \((\Delta \sigma_{ij}, \Delta \varepsilon_{ij})\) are functions of the total strain increment \(\Delta \varepsilon_{ij}\). Differentiating Eqs. (A1) and (A2) with respect to \(\Delta \varepsilon_{ij}\) then gives

\[
\begin{bmatrix}
\delta_{ij} \delta_{kl} - \Delta \tau_{ij} \frac{\partial}{\partial \varepsilon_{ij}} \\
\delta_{ij} \delta_{kl} - \Delta \tau_{ij} \frac{\partial}{\partial \varepsilon_{ij}}
\end{bmatrix}
\begin{bmatrix}
\Delta \varepsilon_{ij} \\
J_{klmn}
\end{bmatrix}
= \begin{bmatrix}
0 \\
\delta_{ijkl}
\end{bmatrix}
\]

(A14)

\(J_{klmn}\) in the above equation is the Jacobian. When computing the Jacobian, all the quantities within the leading square matrices are determined using the values computed in the final iteration for the determination of the stress increment.

**Appendix B. Analytical expressions for the Gibbs free energy and rate potential for the two degree of freedom model of Section 5.**

In this appendix we derive equations for the Gibbs free energy and rate potential for the model of Section 5. These expressions can be differentiated to create the expressions required for the system of rate equations represented by Eq. (41)

**B.1. Determination of Gibbs free energy**

The Gibbs free energy has contributions from the interfacial free energy and elastic stored energy and is given by

\[ G = G_i + U \]  

(B1)

where \(G\) is the Gibbs free energy density, \(G_i\) is the interfacial energy density and \(U\) is the elastic strain energy density of the TBC.

**B.1.1. Determination of interface free energy**

The interfacial energy of the TBC has contributions from bulk contacts associated with \(u_{cl}\) within a cluster and contacts associated with the primary imperfection \(u_{cr}\). Let \(G_{cl}\) be the interface energy density associated with bulk contacts and \(G_{cr}\) be the interface energy density associated with the primary imperfection. Thus \(G_i\) of the TBC becomes

\[ G_i = G_{cl} + G_{cr} \]

(B2)

It can be seen from the Fig. 11b that the local contacts at the primary imperfection characterised by \(u_{cr}\) are not uniform over the entire height of the cluster. The relative displacement of the columns varies linearly with \(x_3\) from the substrate up to a height \(\xi\) and remains constant thereafter, i.e.

\[
\begin{align*}
\dot{u}_{cr}^b &= (u_{cr}^b - u_{cr}^{b0} + u_{cl})(1 - \xi) + u_{cr}^{b0} + \frac{\dot{u}_{cr}^{b0}}{\xi} & \text{if } 0 \leq x_3 < \xi; \\
\dot{u}_{cr} &= u_{cr} & \text{if } \xi \leq x_3 < H.
\end{align*}
\]

(B3)

where a superscript \(b\) refers to the bottom of the imperfection and a superscript \(r\) to the top.

Accordingly, \(G_{cr}\) is the sum of the interface energy density associated with linearly varying contact \(u_{cr}^b(x_3)\) in the bottom portion of the imperfection and that associated with uniform contact \(u_{cr}\) in the top portion. \(G_{cr}\) now becomes

\[ G_{cr} = \int_0^\xi G_{cr}^b \, dx_3 + G_{cr}^r \]

(B4)

Consider a slice of thickness \(\lambda\) of the repeating cell of size \(2R \times 2R\) in the \(x_3\) direction. The interfacial energy density associated with bulk contacts \(G_{cl}\) of the entire cluster can be written in terms of the surface energy \(\gamma_s\) and interfacial energy at the contacts \(\gamma_{bc}\):

\[ G_{cl} = \frac{8R(\frac{b_{c}}{1} - \frac{1}{2})}{4R^2} \left[ 2l_{ci} \gamma_s + 2l_{ci} \gamma_s + (\lambda - 2l_{ci}) \gamma_{bc} \right] \]

(B5)

\(b_{ci}\) and \(l_{ci}\) are equivalent to \(b_1\) and \(l_1\), respectively, given by Eq. (3). The interfacial energy density in the bottom portion of an imperfection is given by

\[ G_{cr}^b = \frac{4R}{\lambda^2} \int_0^\xi \left[ \lambda - \left( \lambda - 2l_{ci} \right) \gamma_s \right] dx_3 \]

(B6)

where \(u_{cr}^b\) is given by the first of Eq. (B3).

Again, the interfacial energy density in the top portion of the imperfection, where there is uniform contact, is given by

\[ G_{cr}^r = \frac{4R(H - \xi)}{4R^2 H_3} \left[ \lambda - \left( \lambda - 2l_{ci} \right) \gamma_s \right] + \gamma_s \left( \frac{\beta}{\lambda} \right) \]

(B7)

Now the total interface energy density of the TBC, \(G_i\), is obtained by adding Eqs. (B5)–(B7)

\[ G_i(u_{cr}, u_{cl}) = G_{cl}(u_{cl}) + G_{cr}^b(u_{cr}, u_{cl}) + G_{cr}^r(u_{cr}) \]

(B8)

This equation can be differentiated with respect to time to give an expression for \(\dot{G}\) which is linear in the rates \(\dot{u}_{cr}, \dot{u}_{cl}\).
B.1.2. Determination of elastic stored energy within cluster

The elastic strain energy in the potential cluster has contributions from field 1, field 2 of Fig. 11 and the interaction between them. As in the analysis of Hutchinson et al. (2006) we assume for simplicity that the TBC is elastically incompressible. The total elastic strain energy $U_c$ in the cluster for an elastically incompressible TBC can be written as

$$U_c = \frac{E}{3} \int e_{ij} e_{ij} dV$$  \hspace{1cm} (B9)

Here, $i$ and $j$ independently range over 1–3. The total elastic strain tensor $e_{ij}$ can be decomposed into strain tensors in field 1 and field 2, i.e.

$$e_{ij} = e_{ij}^1 + e_{ij}^2$$  \hspace{1cm} (B10)

Inserting $e_{ij}$ in the expression for $U_c$, gives

$$U_c = \frac{E}{3} \int e_{ij}^1 e_{ij}^1 dV + \frac{E}{3} \int e_{ij}^2 e_{ij}^2 dV + \frac{2E}{3} \int e_{ij}^1 e_{ij}^2 dV$$  \hspace{1cm} (B11)

The first two terms in the above expression are the strain energy in field 1, $U^1$, and field 2, $U^2$, respectively. The third term is the strain energy due to interaction between the two fields $U^{12}$. The elastic strain tensor in field 1 is obtained using the compatibility condition given by Eq. (30). Consequently, the stored elastic strain energy in field 1 of the TBC cluster is given by

$$U^1 = 8E R^2 H(\epsilon^+ + \epsilon^{s1})^2$$  \hspace{1cm} (B12)

The elastic strain energy in field 2 of the square cluster $U^2$ is estimated by assuming that the cluster is given a uniform in-plane, stress-free transformation strain of $\epsilon^{s2}$, with full constraint against in-plane motion imposed along the bottom surface, $x_3 = 0$. An Eshelby-type cut-and-paste procedure implies that the elastic component of in-plane displacements at the base of the column, $x_3 = 0$, are

$$u_1 = -\epsilon^{s2} x_1; \quad u_2 = -\epsilon^{s2} x_2$$  \hspace{1cm} (B13)

where $x_1$ and $x_2$ are the in-plane co-ordinates from the centreline of the cluster. In order to estimate the elastic strain energy in the cluster it is envisaged that elastic straining occurs over a height $\zeta$ of the TBC coating from the rigid substrate. We assume the following, simple, kinematically admissible field which satisfies this boundary condition as shown in Fig. 11.

$$u_1(x_1,x_3) = \begin{cases} 
-\epsilon^{s2} \left(1 - \frac{x_1}{\zeta}\right) x_1 & \text{if } 0 \leq x_3 \leq \zeta; \\
0 & \text{if } \zeta < x_3 \leq H.
\end{cases}$$

$$u_2(x_2,x_3) = \begin{cases} 
-\epsilon^{s2} \left(1 - \frac{x_2}{\zeta}\right) x_2 & \text{if } 0 \leq x_3 \leq \zeta; \\
0 & \text{if } \zeta < x_3 \leq H.
\end{cases}$$  \hspace{1cm} (B14)

The elastic displacement in the $x_3$ direction is obtained using the elastic incompressibility condition $\epsilon^{s2}_{kk} = 0$

$$u_3(x_3) = \begin{cases} 
\epsilon^{s2} \left(2 x_3 - \frac{2 x_3^2}{\zeta}\right) & \text{if } 0 \leq x_3 \leq \zeta; \\
\epsilon^{s2} \frac{x_3}{\zeta} & \text{if } \zeta < x_3 \leq H.
\end{cases}$$  \hspace{1cm} (B15)

Substituting the resulting strains into (B11) gives the strain energy in field 2 of the cluster

$$U^2 = \frac{E}{2} \int_{-R}^{R} \int_{-R}^{R} \int_{0}^{\zeta} (\epsilon^{s2})^2 \left[4 \left(1 - \frac{x_3}{\zeta}\right)^2 + \frac{1}{3} \left(\frac{x_1^2}{\zeta} + \frac{x_2^2}{\zeta^2}\right)\right] dx_1 dx_2 dx_3$$  \hspace{1cm} (B16)

and the interaction term becomes

$$U^{12} = 4E \int_{-R}^{R} \int_{-R}^{R} \int_{0}^{\zeta} (\epsilon^{s1} + \epsilon^+)^2 \left(1 - \frac{x_3}{\zeta}\right) dx_1 dx_2 dx_3$$  \hspace{1cm} (B17)

Now the total stored elastic strain energy in the cluster is the sum of $U^1$, $U^2$ and $U^{12}$ given by Eqs. (B12), (B16) and (B17), respectively,

$$U_c = 8E R^2 H(\epsilon^+ + \epsilon^{s1})^2 + \frac{8}{3} ER^2 (\epsilon^{s2})^2 \left(1 + \frac{R^2}{6\zeta}\right) + 8E R^2 \zeta (\epsilon^+ + \epsilon^{s1}) \epsilon^{s2}$$  \hspace{1cm} (B18)

The optimal height $\zeta$ that minimises the total strain energy $U_c$ is a function of $\epsilon^{s1}$ and $\epsilon^{s2}$. However, we take $\zeta = R/\sqrt{6}$ which minimises the strain energy in field 2 in order to keep the description of the evolving crack geometry simple. The validity of this assumption can be assessed by comparing the predictions of this model with the finite element studies.
described in Section 4. Therefore, the strain energy density of the TBC becomes

\[ U = 2E(e^{T} + e^{1})^2 + \frac{4}{3\sqrt{6}} H (e^{2})^2 + \frac{2}{\sqrt{6}} \frac{ER}{H} (e^{T} + e^{1})e^{2} \]  

(B19)

The expressions for \( e^{1} \) given by Eq. (35) and \( e^{2} \) given by Eq. (34) in terms of state variables \((u_{cr}, u_{cl})\) can now be used in Eq. (B19) to express the strain energy density \( U \) in terms of the state variables. This can be combined with (B8) to give the total Gibbs free energy density for the system

\[ G(u_{cr}, u_{cl}) = G_{cl}(u_{cl}) + G_{cr}^{b}(u_{cr}, u_{cl}) + G_{cr}^{c}(u_{cr}) + U(u_{cr}, u_{cl}) \]  

(B20)

### B.2. Determination of rate potential at the imperfection and in the cluster

We now can express the dissipation potential from bulk contacts characterised by \( u_{cl} \) in the whole cluster as

\[
\Psi_{cl}^{I} = L_{cl}^{I}(\frac{H}{Z}) \left[ \frac{1}{2} \int_{x=0}^{x=b_{cl}} (-u_{cl}s_{1})^2 \, ds_{1} + \frac{1}{2} \int_{y=0}^{y=l_{cl}} \left( s_{2}(u_{cl} + w_{cl}) \cos \beta - \frac{s_{2}_{b}}{2l_{cl}} (b_{cl} \sin \beta + w_{cl} \cos \beta) \right)^2 \, ds_{2} \right] 
\]

(B21)

where \( L_{cl}^{I} \) is the bulk contact length and the local contact co-ordinates \( s_{1} \) and \( s_{2} \) are defined in Fig. 4b. Simplifying the above expression and dividing by the volume of the cluster yields

\[
\Psi_{cl}^{I}(u_{cl}) = K_{1} u_{cl}^2 \left[ \lambda - \sqrt{\lambda^2 - 4\lambda u_{cl} \cot \beta} \right]^2 \left( D_{l} \lambda \cos \beta + (D_{g} - D_{l} \cos \beta) \sqrt{\lambda^2 - 4\lambda u_{cl} \cot \beta} \right) 
\]

(B22)

where \( K_{1} = (2R - d)/24RdD_{l}D_{g} \cos \beta \).

The expression for \( \Psi_{cl}^{I}(u_{cl}) \) given by Eq. (B22) is the dissipation from bulk contacts in the whole cluster per unit volume and is a quadratic function of \( u_{cl} \). The dissipation from contacts along the imperfection in the bottom portion of the cluster is

\[
\Psi_{cl}^{b} = \frac{4R}{\lambda} \int_{0}^{\zeta} \left[ \frac{1}{2} b_{b}^{e} \int_{0}^{b_{b}} (-u_{cl}s_{1})^2 \, ds_{1} + \frac{1}{2} \int_{0}^{l_{cl}} \left( s_{2}(u_{cl} + w_{cl}) \cos \beta - \frac{s_{2}_{b}}{2l_{cl}} (b_{cl} \sin \beta + w_{cl} \cos \beta) \right)^2 \, ds_{2} \right] \, dz 
\]

(B23)

where \( b_{b}^{e}, w_{b}^{e} \) are related to \( \dot{u}_{cl}^{b}, \dot{w}_{cl}^{b} \) through Eq. (3) and \( \dot{u}_{cl}^{b} \) is given by the first of Eq. (B3).

Manipulating the above expression and dividing it by the volume of the cluster results in the following expression:

\[
\Psi_{cl}^{b} = \int_{0}^{\zeta} \psi_{cl}^{b}(u_{cl}, \dot{u}_{cl}, x_{3}) \, dx_{3} 
\]

(B24)

The function given by Eq. (B24) needs to be integrated numerically. Further, the dissipation in the top portion of the cluster at the imperfection over the height \((H - \zeta)\) is given by

\[
\Psi_{cl}^{t} = \frac{4R(H - \zeta)}{\lambda} \left[ \frac{1}{2} b_{t}^{e} \int_{0}^{b_{t}} (-u_{cl}s_{1})^2 \, ds_{1} + \frac{1}{2} \int_{0}^{l_{cl}} \left( s_{2}(u_{cl} + w_{cl}) \cos \beta - \frac{s_{2}_{b}}{2l_{cl}} (b_{cl} \sin \beta + w_{cl} \cos \beta) \right)^2 \, ds_{2} \right] 
\]

(B25)

where \( b_{t}, w_{t} \) are related to \( \dot{u}_{cl} \) through Eq. (3).

Manipulating the above expression and dividing by the volume of the cluster, we obtain

\[
\Psi_{cl}^{t}(u_{cl}) = K_{2} u_{cl}^2 \left[ \lambda - \sqrt{\lambda^2 - 4\lambda u_{cl} \cot \beta} \right]^2 \left( D_{l} \lambda \cos \beta + (D_{g} - D_{l} \cos \beta) \sqrt{\lambda^2 - 4\lambda u_{cl} \cot \beta} \right) 
\]

(B26)

where \( K_{2} \) is

\[
K_{2} = \frac{(H - \zeta)}{144RH^{2}D_{g}D_{l} \cos \beta} 
\]

(B27)

The macroscopic rate potential per unit volume of the TBC is obtained by adding Eqs. (B22), (B24) and (B26), i.e.

\[
\Psi(\dot{u}_{cl}, \dot{u}_{cl}) = \Psi_{cl}^{I}(\dot{u}_{cl}) + \int_{0}^{\zeta} \Psi_{cl}^{b}(\dot{u}_{cl}, \dot{u}_{cl}, x_{3}) \, dx_{3} + \Psi_{cl}^{t}(\dot{u}_{cl}) 
\]

### Appendix C. Analytical expressions for the three degree of freedom problem

In this appendix we repeat the analysis of Section 5 for the situation where there are two families of imperfections. We start by developing a set of kinematic relationships which relate the sintering strain associated with the three fields described in Section 6 with the three fundamental degrees of freedom for the problem. We then derive relationships for the Gibbs free energy and rate potential.
C. Kinematic coupling between local and global scales

Uniform macroscopic sintering strains, \( \varepsilon^1 \) in field 1, \( \varepsilon^2 \) in field 2 and \( \varepsilon^3 \) in field 3 of the cluster are formulated as functions of primary unknowns \((ucr, ucl, ucr2)\). The unknown variable at the bulk contacts in the cluster \( ucl \) can be written as

\[
u_{cl} = u_{cl}^{0}-(\varepsilon^{1}+\varepsilon^{2}+\varepsilon^{3})d; \quad 0 \leq x_{3} \leq H
\]  
(C1)

The local approach \( u_{cr}(x_{3}) \) at the primary imperfection is given by

\[
u_{cr}(x_{3}) = u_{cr}^{0}-(\varepsilon^{1}+\varepsilon^{2}+\varepsilon^{3})d+\Delta u_{cr}^{l}(x_{3})+\Delta u_{cr2}^{l}(x_{3}); \quad \xi \leq x_{3} \leq H
\]  
(C2)

and the local approach at the secondary imperfection \( u_{cr2}(x_{3}) \) is given by

\[
u_{cr2}(x_{3}) = u_{cr2}^{0}-(\varepsilon^{1}+\varepsilon^{2}+\varepsilon^{3})d+\Delta u_{cr2}^{l}(x_{3}); \quad \xi \leq x_{3} \leq H
\]  
(C3)

Using the compatibility condition in the sub-cluster given by Eq. (40) and considering a kinematically admissible displacement field in each of the sub-clusters, we obtain

\[
\Delta u_{cr2}^{l}(x_{3}) = \begin{cases} 
R \xi^{3} / \xi & \text{if } 0 \leq x_{3} \leq \xi; \\
R \xi^{3} / x_{3} & \text{if } \xi \leq x_{3} \leq H.
\end{cases}
\]

(C4)

Now using \( \Delta u_{cr}^{l}(x_{3}) \) and \( \Delta u_{cr2}^{l}(x_{3}) \) in Eqs. (C2) and (C3) at \( x_{3} = \xi \) and manipulating the resulting expressions for \( u_{cr} \) and \( u_{cr2} \) with \( u_{cl} \) given by Eq. (C1), we can express the sintering strains as functions of the three state variables \((ucr, ucl, ucr2)\) as follows:

\[
\varepsilon^{1} = \frac{u_{cl}^{0} - u_{cl}}{d} - \left[ \frac{(u_{cr} - u_{cr2}) - (u_{cr}^{0} - u_{cr2})}{2R} + \frac{(u_{cl}^{0} - u_{cr2}) - (u_{cl} - u_{cr2})}{R} \right]
\]

(C5)

\[
\varepsilon^{2} = \frac{(u_{cr} - u_{cr2}) - (u_{cr}^{0} - u_{cr2})}{2R}
\]

(C6)

\[
\varepsilon^{3} = \frac{(u_{cl}^{0} - u_{cr2}) - (u_{cl} - u_{cr2})}{R}
\]

(C7)

Note that \( u_{cl}^{0}, u_{cr}^{0}, \) and \( u_{cr2}^{0} \) are the initial values of the kinematic variables \( u_{cl}, u_{cr}, \) and \( u_{cr2} \), respectively, immediately after deposition.

C.2. Determination of Gibbs free energy \( G \)

C.2.1. Determination of interface free energy

We now determine the interface energy density \( G_{i} \) of the TBC. Let \( G_{cl} \) be the interface energy density associated with the bulk contacts, \( G_{cr} \) the interface energy density of the primary imperfections and \( G_{cr2} \) the interface energy density of secondary imperfections of the TBC. Thus \( G_{i} \) of the TBC becomes

\[
G_{i} = G_{cl} + G_{cr} + G_{cr2}
\]

(C8)

\( G_{i} \) in the Eq. (C8) is the same as \( G_{i} \) in the two DOF problem. It can be seen (from the Fig. 19a and b) that the local contact at the secondary imperfection characterised by \( u_{cr2} \) also varies linearly with \( x_{3} \) from the substrate up to a height \( \xi \) and remains constant thereafter over the rest of the height of the TBC as described below

\[
u_{cr2}^{b} = (u_{cr2}^{0} - u_{cl}^{0} + u_{cl}) \left( 1 - \frac{x_{3}}{\xi} \right) + u_{cr2} \frac{x_{3}}{\xi} \quad \text{if } 0 \leq x_{3} \leq \xi;
\]

\[
u_{cl}^{b} = u_{cr2}
\]

(C9)

Accordingly, \( G_{cr2} \) is the sum of interface energy density associated with the linearly varying contacts in the bottom of the cluster characterised by \( u_{cr2}^{b} \) and that associated with uniform contact geometry in top of the cluster characterised by \( u_{cr2}^{c} \). \( G_{cr2} \) now becomes

\[
G_{cr2} = \int_{0}^{\xi} C_{cr2}^{b}(u_{cr2}, u_{cl}) dx_{3} + C_{cr2}^{c}(u_{cr2})
\]

(C10)

Consider a slice of thickness \( \lambda \) of the repeating cell of size \( 2R \times 2R \) in the \( x_{3} \) direction. The interfacial energy density associated with bulk contacts of the entire cluster can be written (see Fig. 19) as

\[
G_{cl} = \frac{2}{\lambda R} \left( \frac{R}{d} - 1 \right) \left[ \left( \sqrt{\lambda^{2} - 4\lambda u_{cl} \cot \beta} \right) (\gamma_{s} - \gamma_{c}) + \gamma_{s} \left( \sec \beta \sqrt{\lambda^{2} - 4\lambda u_{cl} \cot \beta + \lambda} \right) \right] dx_{3}
\]

(C11)
displacement fields 2 and 3 are shown in Fig. 19. The elastic strain tensors in fields 1 and 2 of this problem are exactly Eqs. (B12), (B16) and (B17), respectively. Now, we need to find the strain tensor of field 3, to find the elastic energy due to field 3 in the cluster and the energies due to its interaction with fields 1 and 2. The elastic strain energy in the potential cluster has contributions from fields 1, 2 and 3 and the interaction between them. The total elastic strain energy

\[ C_{\text{el}} = \sum_{i=1}^{3} \int \epsilon_{ij} \sigma_{ij} \, dV \]  

C.2.2. Determination of elastic stored energy within the cluster

The effective contact length at the secondary imperfection is 4R. The interfacial energy density at the secondary imperfection in the bottom portion of the cluster is given by

\[ G_{\text{cr}} = \frac{4R}{4R^2 H} \int \left( \frac{1}{\sqrt{\lambda}} \right) \left( \lambda - \sqrt{\lambda^2 - 4\lambda u_{cr}^2 \cot \beta} \right) \left( \gamma_{1} - \gamma_{2} \right) \, dV \]  

Inserting the first of Eqs. (C9) for \( u_{cr}^2 \) in Eq. (C12) and performing the integration taking \( \xi = \frac{R}{\sqrt{\lambda}} \) yields an explicit analytical expression for \( G_{\text{cr}} \) as a function of \( (u_{cr}, u_{cl}) \). Again, the interfacial energy density in the top portion of the secondary imperfection where there is uniform contact is given by

\[ G_{\text{cr}} = \frac{4R}{4R^2 H} \left( \frac{H - \xi}{\xi} \right) \left( \lambda - \sqrt{\lambda^2 - 4\lambda u_{cr} \cot \beta} \right) \left( \gamma_{1} - \gamma_{2} \right) \, dV \]  

Now the total interface energy density of the TBC is obtained by adding Eqs. (B6), (B7), (C11), (C12) and (C13)

\[ G_{\text{cr}}(u_{cr}, u_{cl}, u_{cr}) = G_{\text{cr}}(u_{cr}, u_{cl}^1) + G_{\text{cr}}(u_{cl}^1) + G_{\text{cr}}(u_{cl}) + G_{\text{cr}}(u_{cr}^2, u_{cl}^1) + G_{\text{cr}}(u_{cr}^2, u_{cl}) \]  

C.2.2. Determination of elastic stored energy within the cluster

The elastic strain energy in the potential cluster has contributions from field 1, field 2 and field 3 and the interaction between them. The total elastic strain energy \( U_{\text{c}} \) in an elastically incompressible cluster can be written as

\[ U_{\text{c}} = \frac{E}{3} \int \epsilon_{ij} \epsilon_{ij} \, dV \]  

Here, \( i \) and \( j \) independently range over 1–3. The total elastic strain tensor \( \epsilon_{ij} \) can be decomposed into strain tensors in fields 1, 2 and 3 as

\[ \epsilon_{ij} = \epsilon_{ij}^{1} + \epsilon_{ij}^{2} + \epsilon_{ij}^{3} \]  

Inserting \( \epsilon_{ij} \) in Eq. (C15)

\[ U_{\text{c}} = \frac{E}{3} \int \epsilon_{ij}^{1} \epsilon_{ij}^{1} \, dV + \frac{E}{3} \int \epsilon_{ij}^{2} \epsilon_{ij}^{2} \, dV + \frac{E}{3} \int \epsilon_{ij}^{3} \epsilon_{ij}^{3} \, dV + \frac{2E}{3} \int \epsilon_{ij}^{1} \epsilon_{ij}^{2} \, dV + \frac{2E}{3} \int \epsilon_{ij}^{1} \epsilon_{ij}^{3} \, dV + \frac{2E}{3} \int \epsilon_{ij}^{2} \epsilon_{ij}^{3} \, dV \]  

The terms 1, 2 and 3 in Eq. (C17) represent the elastic strain energy due to fields 1, 2 and 3, respectively. The fourth, fifth and sixth terms represent the energy due to interactions between strain fields 1–2, 2–3 and 3–1, respectively. The displacement fields 2 and 3 are shown in Fig. 19. The elastic strain tensors in field 1 and field 2 of this problem are exactly the same as the strain tensors in field 1 and field 2 of the two state variable problem described in Appendix B. The elastic strain energy due to field 1 of the cluster, \( U^{1} \), that due to field 2 of the cluster, \( U^{2} \), and their interaction, \( U^{12} \), are given by Eqs. (B12), (B16) and (B17), respectively. Now, we need to find the strain tensor of field 3, \( \epsilon_{ij}^{3} \), in each sub-cluster in order to find the elastic strain energy due to field 3 in the cluster and the energies due to its interaction with fields 1 and 2. The elastic strain tensor in the bottom of each sub-cluster of field 3 which contributes to elastic stored energy is given by

\[ \epsilon_{ij}^{3}(x_1, x_2, x_3) = \begin{bmatrix} -\rho^{3} \left( 1 - \frac{x_1}{z_1} \right) & 0 & \rho^{3} \left( \frac{x_1 - z_1}{z_2} \right) \\ 0 & -\rho^{3} \left( 1 - \frac{x_2}{z_2} \right) & \rho^{3} \left( \frac{x_2 - z_2}{z_3} \right) \\ \rho^{3} \left( \frac{x_1 - z_1}{z_2} \right) & \rho^{3} \left( \frac{x_2 - z_2}{z_3} \right) & 2\rho^{3} \left( 1 - \frac{x_3}{z_3} \right) \end{bmatrix} \]
The elastic strain energy due to field 3 in the cluster is

\[ U^3 = \frac{2}{3} ER^2 \left( \frac{\varepsilon^3}{\varepsilon} \right)^2 \left( 4 \varepsilon + \frac{R^2}{6\varepsilon} \right) \]  

(C19)

The elastic strain energy due to interaction between fields 2 and 3 is

\[ U^{23} = \frac{2}{9} ER^2 \delta^2 \varepsilon^3 \left( 24\varepsilon + \frac{R^2}{\varepsilon} \right) \]  

(C20)

The strain energy due to interaction between fields 3 and 1 is

\[ U^{31} = 8E R^2 \xi (\varepsilon^T + \varepsilon^1) \varepsilon^3 \]  

(C21)

Now, the total elastic strain energy in the cluster is

\[ U_c = 8ER^2 H (\varepsilon^T + \varepsilon^1)^2 + \frac{8}{3} ER^2 (\varepsilon^2)^2 \left( \frac{\varepsilon^2}{\varepsilon} + \frac{R^2}{6\varepsilon} \right) + \frac{2}{3} ER^2 (\varepsilon^3)^2 \left( \frac{4 \varepsilon^2 + \frac{R^2}{6\varepsilon}}{\varepsilon} \right) + 8ER^2 \xi (\varepsilon^T + \varepsilon^1) \varepsilon^3 \]  

(C22)

Setting \( \xi = R/\sqrt{6} \), as before, the strain energy density of the TBC becomes

\[ U = 2Ec^T + \frac{ER}{9} \left( \frac{\varepsilon^2}{\varepsilon} + \frac{5\sqrt{6}}{36} (\varepsilon^3)^2 + \frac{\sqrt{2}}{3} (\varepsilon^T + \varepsilon^1)^2 + \frac{5\sqrt{6}}{18} c^2 \varepsilon^3 + \frac{2}{\sqrt{6}} (\varepsilon^T + \varepsilon^1) \varepsilon^3 \right) \]  

(C23)

The expressions for \( \varepsilon^1 \) given by Eq. (C5), \( \varepsilon^2 \) given by Eq. (C6) and \( \varepsilon^3 \) given by Eq. (C7) in terms of state variables can now be used in Eq. (C23) to express the strain energy density \( U \) in terms of state variables \((u_{cr}, u_{cl}, u_{cr})\). Now the Gibbs energy density \( G \) can be obtained by adding \( U \) to \( G_0 \) given by Eq. (C14)

\[ G(u_{cr}, u_{cl}, u_{cr}) = C_{cr}^0 (u_{cr}, u_{cl}) + C_{cr}^0 (u_{cr}) + G_{cr}(u_{cl}) + G_{cr}^b (u_{cr}, u_{cl}) + G_{cr}^b (u_{cr}) + U(u_{cr}, u_{cl}, u_{cr}) \]  

(C24)

### C.3. Determination of dissipation potential at the imperfection and in the cluster

Similar to the two state variable problem of Appendix B, we can now find the macroscopic dissipation potential per unit volume of the TBC (see Fig. 19). The dissipation from bulk contacts in the whole cluster per unit volume is given by

\[ \psi_{cr}(u_{cr}) = \int_0^\xi \psi_{cr}^b (u_{cr}, u_{cl}, x_3) dx_3 \]  

(C26)

Further, the dissipation in the top portion of cluster at the secondary imperfection where there is uniform contact over height \( H + \xi \) can be given by

\[ \psi_{cr}^t (u_{cr}, u_{cl}) = K_2 u_{cr}^2 \left[ \lambda - \sqrt{\lambda^2 - 4\lambda u_{cr} \cot \beta} \right] \left( D_s \lambda \cos \beta + (D_e - D_s \cos \beta) \sqrt{\lambda^2 - 4\lambda u_{cr} \cot \beta} \right) \]  

(C27)

Now the macroscopic dissipation potential per unit volume of TBC is given as the sum of Eqs. (B24), (B26), (C25), (C26) and (C27):

\[ \psi (u_{cr}, u_{cl}, u_{cr}) = \psi_{cr}(u_{cr}) + \int_0^\xi \psi_{cr}^b (u_{cr}, u_{cl}, x_3) dx_3 + \psi_{cr}^t (u_{cr}) + \int_0^\xi \psi_{cr}^b (u_{cr}, u_{cl}, x_3) dx_3 + \psi_{cr}^t (u_{cr}) \]  

(C28)

The second and third terms in Eq. (C28) need to be numerically integrated at each time step during the solution process. In the simulations presented here a two point Gaussian integration scheme was employed.

### References


