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Effect of surface energy on the yield strength of nanoporous materials

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The effect of surface energy on the yield strength of nanoporous materials is investigated in this letter. The conventional micromechanics method is extended to consider the surface effect and expression of effective yield surface of nanoporous materials in complex stress state is derived. It is seen that surface energy has significant effect on the yield strength of nanoporous materials, and the smaller the nanosized void, the more significant the effect of surface energy. The yield strength of nanoporous materials has size-dependent effect.

Investigation of the mechanical properties of solids with nanosized inhomogeneities (e.g. nanoparticle composites[1], nanoporous materials[2], etc.) is of great interest to materials science, solid state physics, nanotechnology, etc. Due to the increased ratio of surface to bulk volume, the effect of surface energy becomes significant at nanoscale and is attributed to the size-dependent properties of nanosized elements[3, 4]. Recently, the effect of surface energy on the elastic behavior of solids is extensively investigated, such as the elastic properties of nanoparticles, wires and films[5], the elastic deformation near nanosized spherical and elliptical inhomogeneities[6, 7], and the effective moduli of solids with nanoinclusions[8, 9], etc.

Until now, little attention is devoted to the surface effect on the elastic limit i.e. the yield strength of nanomaterials. In what follows, according to the usual practice in engineering, we name the elastic limit as yield strength. Yield strength is an important parameter of solids. Even for a material or a structure with high Young's modulus, its application may be limited by its yield strength [10]. If the applied stress is less than the

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yield strength of materials, the deformation is elastic, otherwise, an irrecoverable plastic deformation and/or failure will occur. Up to now, the effect of surface energy on the yield strength of solids with nanosized inhomogeneities is not yet clear. Therefore, it is imperative to investigate the effect of surface energy on the yield strength of solids with nanosized inhomogeneities.

We consider the case that the spherical nanovoids are identical in size and uniform distributed in the matrix. The nanoporous material as a whole is isotropic. The yield of porous material is because of the local equivalent stress in the matrix reaching its yield stress. When applying arbitrary load to the porous material, our aim is to find out the local equivalent stress in the matrix and judge if it reaches the critical yield stress. All the macroscopic stresses resulting in the local yield build up a surface in the stress space i.e. the yield surface or the yield locus of the porous material. In what follows we adopt the field fluctuation method proposed by Qiu and Weng [11] and Hu [12] to obtain the yield surface of the nanoporous material.

To consider the surface energy of nanosized voids, the surface elasticity theory presented by Gurtin *et al.*[13] is adopted, which is experimentally verified to agree well with directly atomic simulation [4, 14, 15]. Here, we neglect the influence of residual stress field on the yield strength and only consider the influence of surface elasticity with an isotropic property. Its two-dimensional shear modulus and compression modulus are m_s and k_s respectively. In the matrix, the classical elasticity theory still holds. The shear modulus and bulk modulus of matrix are m and k respectively. For a representative volume element (RVE) of nanoporous materials, the macroscopic stress $\mathbf{\Sigma}$ and strain $\mathbf{E}$ can be calculated as

$$\mathbf{\Sigma} = \frac{1}{V}\int_{\partial V}\left(\boldsymbol{\sigma}\cdot\mathbf{N}\right)\otimes\mathbf{x}\,\mathrm{d}S \tag{1}$$

$$\mathbf{E} = \frac{1}{2V}\int_{\partial V}\left(\mathbf{N}\otimes\mathbf{u}+\mathbf{u}\otimes\mathbf{N}\right)\mathrm{d}S \tag{2}$$

where $\boldsymbol{\sigma}$ and $\mathbf{u}$ are the microscopic stress and displacement, respectively, $\mathbf{N}$ the unit normal vector on RVE surface, $\mathbf{x}$ the position vector, and V and S the volume and surface area of the RVE, respectively. In this letter, all the bold characters are tensors or vectors.

From the above definitions of macroscopic stress and strain, we obtained the so-called Hill condition for the material with surface/interface energy, which is the basis of our analysis. For the nanoporous materials, the corresponding Hill condition is as follows:

$$\mathbf{\Sigma}:\mathbf{E} = f_1 \langle \boldsymbol{\sigma}:\boldsymbol{\varepsilon} \rangle_1 + \frac{f_0}{V_0} \int_{\partial V_0} \boldsymbol{\tau}:\boldsymbol{\varepsilon}_s \, \mathrm{d}S \tag{3}$$

where $\boldsymbol{\tau}$ and $\boldsymbol{\varepsilon}_s$ are the surface stress and strain, respectively, f_1 the volume fraction of matrix, $\langle \times \rangle_1$ volume average over the matrix, f_0 and V_0 the volume fraction and volume of the voids, respectively. Here, $f_1 + f_0 = 1$. It should be pointed out that $\boldsymbol{\sigma}$ and $\boldsymbol{\varepsilon}$, $\boldsymbol{\tau}$ and $\boldsymbol{\varepsilon}_s$ in Eq. (5) are not necessarily related by the constitutive equation. In fact, Hill's condition is the principle of virtue work for the RVE. If $\boldsymbol{\sigma}$ and $\boldsymbol{\varepsilon}$ are the real stress and strain fields related by constitutive relation, Hill's condition is the energy balance equation

$$2U(\mathbf{\Sigma}) = \mathbf{\Sigma}:\mathbf{M}:\mathbf{\Sigma} = f_1 \langle \boldsymbol{\sigma}:\mathbf{m}:\boldsymbol{\sigma} \rangle_1 + \frac{f_0}{V_0} \int_{\partial V_0} \boldsymbol{\tau}:\mathbf{m}_s:\boldsymbol{\tau} \, \mathrm{d}S \tag{4}$$

where U is the stress energy of the RVE, $\mathbf{M}$ and $\mathbf{m}$ the macroscopic and microscopic compliance tensors of nanoporous material and matrix, respectively, $\mathbf{m}_s$ the surface compliance tensor.

According to the field fluctuation method [12], for a constant macroscopic load applied to the RVE, the variation of microscopic compliance tensor $d\mathbf{m}$ will result in the variation of the microscopic stresses $d\boldsymbol{\sigma}$ and $d\boldsymbol{\tau}$, and then the variation of average stored energy dU and the macroscopic compliance tensor $d\mathbf{M}$ of the nanoporous material, then we have

$$\mathbf{\Sigma}:d\mathbf{M}:\mathbf{\Sigma} = f_1 \langle \boldsymbol{\sigma}:d\mathbf{m}:\boldsymbol{\sigma} \rangle_1 + 2 f_1 \langle \boldsymbol{\sigma}:\mathbf{m}:d\boldsymbol{\sigma} \rangle_1 + 2\frac{f_0}{V_0} \int_{\partial V_i} \boldsymbol{\tau}:\mathbf{m}_s:d\boldsymbol{\tau} \, \mathrm{d}S \tag{5}$$

The last two terms at the right-hand side of Eq. (5) correspond to the virtue work of the RVE under fixed boundary condition and the variation of macroscopic stress is equal to zero. Considering Eq.(3), the last two terms are equal to zero. Then we obtain

$$\mathbf{\Sigma} : d\mathbf{M} : \mathbf{\Sigma} = f_1 \langle \boldsymbol{\sigma} : d\mathbf{m} : \boldsymbol{\sigma} \rangle_1 \tag{6}$$

Let only shear modulus of matrix undergoes a small variation, we then obtain from Eq. (6)

$$f_1 \langle \sigma'_{ij} \sigma'_{ij} \rangle_1 \delta\left(\frac{1}{2\mu}\right) = S'_{ij} S'_{ij} \delta\left(\frac{1}{2G}\right) + S_m^2 \delta\left(\frac{1}{K}\right) \tag{7}$$

where $\sigma'_{ij} = \sigma_{ij} - \sigma_m \delta_{ij}$ is the microscopic deviator stress tensor with $\sigma_m = \frac{1}{3}\mathrm{tr}\,\sigma_{ij}$ being the microscopic hydrostatic stress in the matrix, $S'_{ij} = S_{ij} - S_m \delta_{ij}$ and $S_m = \frac{1}{3}\mathrm{tr}\,S_{ij}$ the macroscopic deviator stress tensor and hydrostatic stress of the nanoporous material, respectively, μ the shear modulus of the matrix, and G and K the macroscopic shear modulus and bulk modulus, respectively. Einstein's summation convention is adopted all repeated indices and i,j=1, 2, 3, respectively. Form Eq.(12) we obtain the relationship between the macroscopic and microscopic stresses,

$$\langle \sigma'_{ij} \sigma'_{ij} \rangle_1 = \frac{1}{f_1}\left\{ \left(\frac{\mu}{G}\right)^2 \frac{\partial G}{\partial \mu} S'_{ij} S'_{ij} + 2\left(\frac{\mu}{K}\right)^2 \frac{\partial K}{\partial \mu} S_m^2 \right\} \tag{8}$$

It should be pointed out that there is essentially difference between eqs.(6)-(8) and those of Hu [12] although they have the same forms apparently, because the surface effect has been included in the effective moduli G and K at the present work.

From Eq.(8), we know that once the macroscopic effective moduli K and G including the surface/interface effect are obtained, the local stress in the matrix can be obtained. There are several methods to obtain the effective moduli. Here we use the results of Duan *et al.*[8]. The expressions of effective moduli are very complex and will not be presented here. In most cases, for porous materials, the bulk deformation of matrix is neglectable compared with the shear deformation. To simplify the problem considered here, we neglect the bulk deformation of matrix i.e. $k \to +\infty$. We obtain the following simplified expressions of the effective moduli of nanoporous materials,

$$K = \frac{4 - 4f_0 + 2k_s^r}{3f_0}\mu \tag{9}$$

$$G = \frac{6(1 - f_0) + 6\mu_s^r(1 + f_0) + k_s^r(4 - 3f_0) + k_s^r\mu_s^r(2 + 3f_0)}{2\left[3 + 2f_0 + \mu_s^r(3 - 2f_0) + k_s^r(2 + f_0) + k_s^r\mu_s^r(1 - f_0)\right]}\mu \tag{10}$$

where $k_s^r = k_s / R\mu$ and $\mu_s^r = \mu_s / R\mu$, R is the radius of voids.

Substituting Eqs (9) and (10) into Eq.(8), we obtain the effective Mises stress

$$\left\langle \sigma_e^2 \right\rangle_1 = \frac{\Sigma_e^2}{A^2} + \frac{\Sigma_m^2}{B^2} \tag{11}$$

where

$$\sigma_e^2 = 3/2\, \sigma_{ij}^{'} \sigma_{ij}^{'},$$

$$A^2 = \left[\frac{1}{f_1} \left(\frac{\mu}{G} \right)^2 \frac{\partial G}{\partial \mu} \right]^{-1} = \frac{\left(V_1 + V_2 f_0 \right)^2 \left(f_0 - 1 \right)}{V_3 f_0^2 + 2\left[6\left(1 + k_s^r \right)^2 + V_4 \right] f_0 + V_5},$$

$$B^2 = \left[\frac{3}{f_1} \left(\frac{\mu}{K} \right)^2 \frac{\partial K}{\partial \mu} \right]^{-1} = \frac{\left(2 - 2 f_0 + k_s^r \right)^2}{9 f_0},$$

with

$$V_1 = 6 + 6\mu_s^r + 4k_s^r + 2k_s^r \mu_s^r,$$

$$V_2 = 3\left(-2 + 2\mu_s^r - k_s^r + k_s^r \mu_s^r \right),$$

$$V_3 = 6\left(k_s^r + 2 \right)^2 \left(\mu_s^r - 1 \right)^2,$$

$$V_4 = -4\left(k_s^r - 6\mu_s^r \right)^2 + 2\mu_s^r \left(69\mu_s^r + 30 \right) + k_s^{r2} \mu_s^r \left(14 - \mu_s^r \right),$$

$$V_5 = -4\left(k_s^r \mu_s^r + 2k_s^r + 3\mu_s^r + 3 \right)^2.$$

Here the matrix obeys Mises yield criterion, i.e. when $\sigma_e = \sigma_{y0}$ with σ_{y0} being the yield strengths of matix, the nanoporous material yields. Thus, the macroscopic yield condition of nanoporous materials can be expressed as

$$F\left(\Sigma_e, \Sigma_m \right) = \frac{\Sigma_e^2}{A^2 \sigma_{y0}^2} + \frac{\Sigma_m^2}{B^2 \sigma_{y0}^2} - 1 = 0 \tag{12}$$

If $F\left(\Sigma_e, \Sigma_m \right) < 0$, deformation of nanoporous material is elastic. If $F\left(\Sigma_e, \Sigma_m \right) > 0$, irrecoverable plastic deformation and yield failure of the material occurs. In the case of uniaxial stress state, when applying the macroscopic stress $\bar{\Sigma}$, the macroscopic Mises stress $\Sigma_e = \bar{\Sigma}$ and the macroscopic hydrostatic stress $\Sigma_m = 1/3\, \bar{\Sigma}$. Then, from Eq. (12) we obtain the uniaxial yield strength Σ_{y0} of nanoporous material

$$\Sigma_{y0}=\sigma_{y0}\left(\frac{1}{A^2}+\frac{1}{9B^2}\right)^{-\frac{1}{2}} \tag{13}$$

It is seen from Eqs. (12) and (13) that the macroscopic yield strength of nanoporous material is affected by the surface energy through parameters k_s^r and μ_s^r, which are size-dependent. If $k_s^r=0$, $\mu_s^r=0$, Eqs (12) and (13) reduce to the yield surface and uniaxial yield strength of porous material without surface effect, respectively.

In what follows, examples of the effect of surface energy on the yield surface in complex stress state and the uniaxial yield strength of nanoporous aluminum are presented, respectively. The shear modulus μ and yield strength σ_{y0} of bulk aluminum are 23GPa and 250MPa, respectively, which are obtained from[14]. The volume fraction f_0 of nanosized voids is assumed to be 10%. We consider two cases of material constants: case 1, $k_s=12.932$ N/m and $\mu_s=-0.3755$ N/m; case 2, $k_s=-5.457$ N/m and $\mu_s=-6.2178$ N/m.

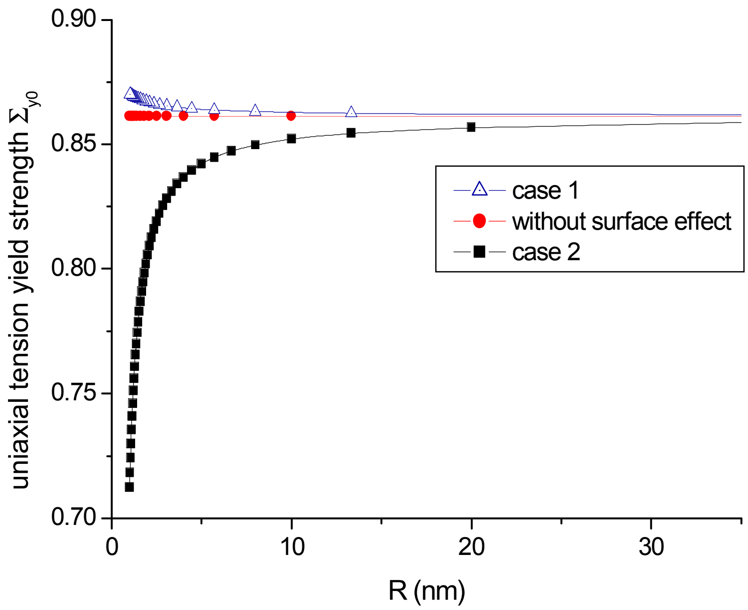

Fig.1. Effect of surface energy on the uniaxial yield strength of nanoporous aluminum with void fraction $f_0=10\%$.

Effect of surface energy on the uniaxial yield strength of the nanoporous aluminum is shown in Fig.1. It is readily seen that surface energy has significant effect on the yield strength of nanoporous materials. For case 1, the nanoporous material has higher value of yield strength than conventional porous material without surface effect, and the yield strength decreases with the increase of the radius of void, particularly when $R < 10nm$. For case 2, the nanoporous material has lower value of yield strength than conventional porous material without surface effect, and the yield strength increases quickly with increase of the radius of void, particularly when $R < 10nm$. This indicates that the yield strength of nanoporous materials is size-dependent.

Effect of surface energy on the yield surface of the nanoporous aluminum in complex stress state is shown in Fig.2. For case 1, nanoporous material has larger yield surface than the conventional porous material without surface effect, and the smaller the radius of nanosized void, the larger the yield surface, particularly when $R < 10nm$. For case 2, the yield surface of nanoporous material is smaller than that of conventional porous material without surface effect. With the decrease of void radius, the yield surface becomes more and more small. The surface effect is significant when $R < 10nm$ and not so clear when $R > 10nm$. For both cases, the yield surface of nanoporous material finally approaches to that of conventional porous material with the increase of void radius.

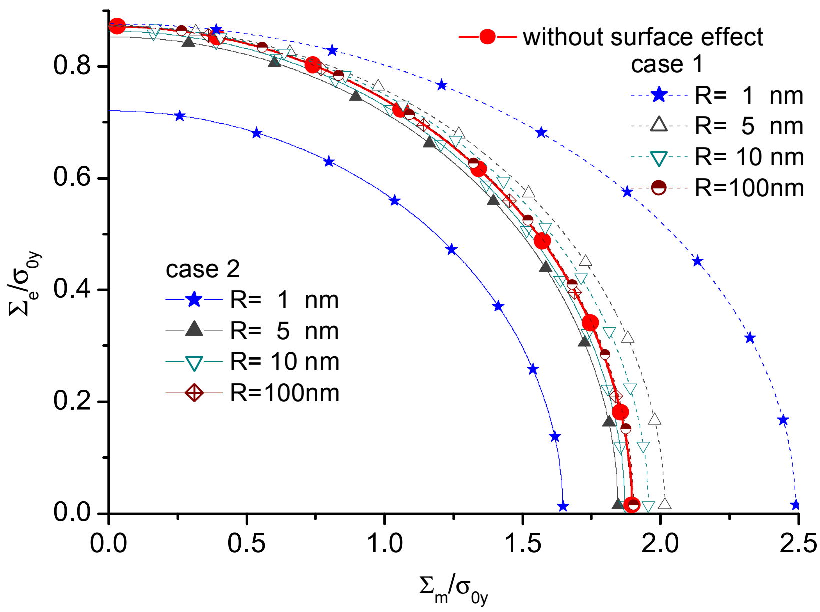

Fig.2. Effect of surface energy on the effective yield surface of nanoporous aluminum with void fraction $f_0 = 10\%$.

In summary, we have extended the conventional micromechanics method[14, 15] to consider the effect of surface energy. The expressions of macroscopic yield surface of nanoporous materials with surface effect are obtained. It can be concluded that the surface energy has significant effect on the yield strength or elastic limit of nanoporous materials when the radius of nanosized void is less than 10*nm*, and the surface effect becomes neglectable when the radius of nanosized void is greater than 10 nm. The yield strength of nanoporous materials has size-dependent effect.

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Appendix：

The surface stress $\boldsymbol{\tau}$ and surface strain $\boldsymbol{\varepsilon}_s$ satisfies a linear constitutive equation

$$\boldsymbol{\tau} = 2m_s\boldsymbol{\varepsilon}^s + l_s\left(\mathrm{tr}\,\boldsymbol{\varepsilon}^s\right)\mathbf{I}^{(2)} \quad (1)$$

Where m_s and l_s are the modulus of void surface, $\mathbf{I}^{(2)}$ is the second-order unit tensor in two-dimensional space. Here all the bold letter are tensor or vector.

The equilibrium and constitutive equations of the matrix is as follows

$$\nabla \cdot \boldsymbol{\sigma} = 0 \qquad (2)$$

$$\boldsymbol{\varepsilon} = \frac{1}{2}\left(\nabla \otimes \mathbf{u} + \mathbf{u} \otimes \nabla\right) \qquad (3)$$

$$\boldsymbol{\sigma} = l\left(\mathrm{tr}\,\boldsymbol{\varepsilon}\right)\mathbf{I}^{(3)} + 2m\boldsymbol{\varepsilon} \qquad (4)$$

where l and m are modulus of matrix, $\mathbf{I}^{(3)}$ is the second-order unit tensor in three-dimensional space. $\mathbf{u}$, $\boldsymbol{\varepsilon}$ and $\boldsymbol{\sigma}$ is the displacement, strain tensor and stress tensor of matrix.

The mechanical equilibrium of the void surface satisfies the generalized Young-Laplace equations for solids

$$\begin{aligned} \mathbf{n} \cdot [\boldsymbol{\sigma}] \cdot \mathbf{n} &= -\boldsymbol{\tau} : \boldsymbol{\kappa} \\ \mathbf{P} \cdot [\boldsymbol{\sigma}] \cdot \mathbf{n} &= -\nabla_s \cdot \boldsymbol{\tau} \end{aligned} \qquad (5)$$

where $\mathbf{P} = \mathbf{I}^{(3)} - \mathbf{n} \otimes \mathbf{n}$, $\mathbf{n}$ is the unit normal vector on the void surface which positive direction is from the void to the matrix. $\nabla_s \cdot \boldsymbol{\tau}$ is the surface divergence of the surface stress $\boldsymbol{\tau}$ and $\boldsymbol{\kappa}$ is the curvature tensor . $[s]$ is the stress jump across the surface from the void to the matrix.