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EVOLUTION OF THE CYLINDRICAL NANOPORE MORPHOLOGY UNDER DIFFUSION PROCESSES

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Abstract. In the present paper, we provide a theoretical approach to the analysis of nanopore morphological stability under diffusion taking into account surface elasticity. It is assumed that the pore shape may change during stress relaxation. The surface atomic flux is caused by the nonuniform distribution of chemical potential, which depends on bulk and surface stresses as well as pore surface curvature. The change in surface relief is described by the linearized evolution equation, which is derived taking into account the solution of the boundary value problem of plane elasticity for determining the elastic and surface energy. For this purpose, we use a first-order approximation of the boundary perturbation method. The solution of the linearized evolution equation allows us to analyze the influence of physical and geometrical parameters of the problem on pore surface morphological stability.

Keywords: 2D problem, nanopore, morphological instability, surface diffusion, boundary perturbation method, nanomaterials.

1. Introduction

The production of porous nanomaterials is of a great interest in connection with their use in the development of filters and sensors for microelectronics [1], which dictates sufficiently stringent requirements for the purity and structure of the pore surface. However, many experimental and theoretical studies have shown that nanoscale grooves and crack-like valleys can be introduced on free surfaces such materials at the stage of fabrication and subsequent thermal or chemical processing [2,3].

Over the last years, it was found that the elastic fields may affect the surface morphological stability of pores, voids, and channels. They may change their shape under internal or external stresses [4]. Morphological change can also affect the behavior of bulk materials initiating the crack nucleation at voids surfaces [5]. The development of plastic deformation and fracture processes largely determines the mechanical properties of the material as a whole and is therefore of great interest [6,7]. On the other hand, the consideration of nanoscale cavities and inclusions in the framework of the classical linear theory of elasticity can lead to inaccuracies in determining the levels of strains and stresses and, consequently, to incorrect dependences of these characteristics on the parameters of the system. To overcome these difficulties, the theory of surface elasticity in which surface and interphase domains are represented as negligibly thin layers ideally adhering to the bulk materials is widely used in recent years [8]. This approach has shown its effectiveness in the analysis of the mechanical properties of nanosized structural elements, such as nanodefects, nanowires, nanobeams, and nanoplates, for example [9,10].

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In the works [11,12], we used the boundary perturbation technique to solve 2D boundary value problem for solids with a nearly circular defect under plane deformation. The obtained results allowed us to estimate the effect of small deviation of the defect boundary from circle one and defect shape on the stress-strain state and, in particular, on the stress concentration. Within the present research, we are going to develop a continuum model of surface defects growth in nanoporous materials that take the thermodynamic processes localized in the surface layers into account. In the proposed model, the growth of the surface topological defects is associated with morphological changes at the atomic level due to stress relaxation mechanism during fabrication, processing, and exploitation of the material. The dominant driving force of such transformations is a change in the chemical potential, which leads to diffusion of atoms along the surface with a high value of the chemical potential to the regions with a low value due to the reduced stability of the surface atomic layers.

The purpose of the present work is to investigate the effect of the surface elastic properties on the stability of the hole shape. We study the evolution of a cylindrical nanopore in a stressed solid using the approaches developed in [12,13]. It is assumed that during stress relaxation the pore changes shape via a mass transport mechanism. The flow of atoms along the surface is caused by a nonuniform distribution of the chemical potential which depends on the stress-strain state of the subsurface layer. The conditions at the boundary are formulated according to the generalized Laplace-Young law [14], and Gurtin-Murdoch's surface elasticity model [8]. Following the work [12], we use Goursat-Kolosov complex potentials and boundary perturbation method to solve the problem. As a result, an equation describing the amplitude change of pore surface perturbation over time is obtained.

2. Statement of the problem

Consider an infinite elastic body with a cylindrical nanopore that is close in shape to the circular cross-section of radius a (Fig. 1). We assume that the plane strain conditions are satisfied and the problem formulated for 2D domain in the plane perpendicular to the cylinder axis, the hole boundary Γ can be approximated by the following parametric equation in polar coordinates (r, θ)

$$\Gamma = \{z: z|_{r=\rho} \equiv \zeta = \rho s = a(1 + \varepsilon(\tau)\cos 2\theta)\, s\}, \quad (1)$$

$$\varepsilon(\tau) = A(\tau)/a,\ A(0) = A_0,\ 0 < A(\tau) \ll a\ \forall\ \tau,$$

where $s = e^{i\theta}$, $z = x_1 + ix_2$ is the complex variable, $i = \sqrt{-1}$ is the imaginary unit, ρ is the polar radius of a point at the hole boundary, $A(\tau)$ is the deviation amplitude of the pore boundary from the circle shape at time τ.

In the case of the plane strain, constitutive relations of the surface and bulk elasticity theory are defined as follows according to [6,8]

$$\sigma_{tt}^s = \gamma_0 + M\,\varepsilon_{tt}^s,\ M = \lambda_s + 2\mu_s, \quad (2)$$

$$\sigma_{nn} = (\lambda + 2\mu)\varepsilon_{nn} + \lambda\varepsilon_{tt},\ \sigma_{tt} = (\lambda + 2\mu)\varepsilon_{tt} + \lambda\varepsilon_{nn}. \quad (3)$$

In Equations (2) and (3), σ_{ij} is the stress tensor component, $\sigma_{tt}^s = q$ is the surface stress, ε_{ij}^s and ε_{ij} are the components of the surface and bulk strain tensors, λ and μ (λ_s and μ_s) are Lame constants of the bulk (surface) material, γ_0 is residual surface stress.

According to the Laplace-Young law, the conditions of mechanical equilibrium at the boundary Γ have the following form [6,11]:

$$\sigma_n(\zeta) = \sigma_{nn} + i\sigma_{nt} = \kappa\sigma_{tt}^s - i\frac{1}{h}\frac{d\sigma_{tt}^s}{d\theta} \equiv t^s(\zeta),\ \zeta \in \Gamma. \quad (4)$$

Here σ_{nn} and σ_{nt} are the components of bulk stress tensor defined in the local coordinates (n, t), where n and t are normal and tangential to the surface of the hole; κ and h are the surface curvature and metric coefficient [15], respectively. At infinity, stresses σ_{ij}^∞ $(i, j = 1, 2)$ and the rotation angle ω of a material particle are specified as

$$\sigma_{11}^\infty = \sigma_{22}^\infty = \sigma_0,\ \sigma_{12}^\infty = 0,\ \omega^\infty = 0. \quad (5)$$

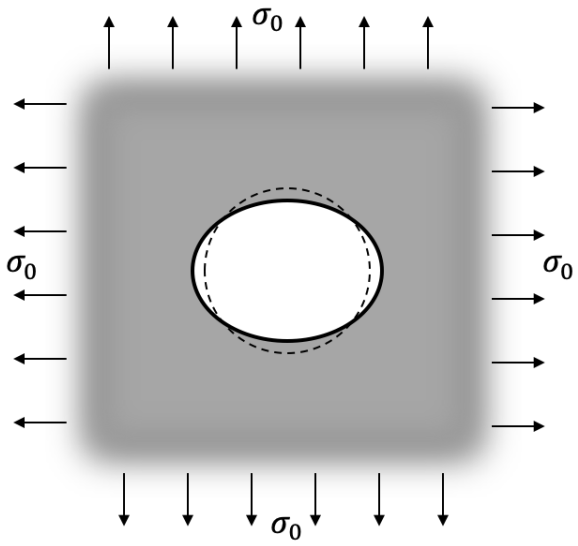

Fig. 1. An elastic medium containing a cylindrical nanopore under biaxial loading

Since we assume that the surface phase and the bulk material are coherently bonded, the inseparability condition can be defined as

$$\varepsilon_{tt}^{s}(\zeta) = \varepsilon_{tt}(\zeta),\ \zeta \in \Gamma. \tag{6}$$

It is expected that due to stress relaxation, the shape of the pore surface may change via surface diffusion. It is required to define the dependence of perturbation amplitude change of pore surface (1) on time τ.

3. Boundary perturbation procedure and linear stability analysis

The atomic flux along the pore boundary Γ is proportional to the gradient of the chemical potential χ [16]

$$J(\zeta,\tau) = -\frac{D_s C_s}{k_b T}\frac{\partial \chi(\zeta,\tau)}{\partial s}, \tag{7}$$

where D_s is the self-diffusivity coefficient; C_s is the number of diffusing atoms per unit area; k_b is the Boltzmann constant, T is the absolute temperature and s is arc length along Γ.

The local chemical potential χ is considered as free energy per unit of added volume [17]

$$\chi(\zeta,\tau) = \chi_0 + [U(\zeta,\tau) - \kappa(\zeta,\tau)U_s(\zeta,\tau)]\Omega, \tag{8}$$

where χ_0 is the constant local chemical potential of stress-free circle pore, Ω is the atomic volume, U is the strain elastic energy density and U_s is the surface energy.

The mass conservation law and Eqs. (7) and (8) give the change of pore surface profile

$$g(\theta,\tau) = A(\tau)\cos(2\theta), \tag{9}$$

in the form of the evolution equation

$$\frac{\partial g(\theta,\tau)}{\partial \tau} = K_s h(\zeta,\tau)\frac{\partial^2}{\partial s^2}[U(\zeta,\tau) - \kappa(\zeta,\tau)U_s(\zeta,\tau)],\ K_s = D_s C_s \Omega^2/(k_b T). \tag{10}$$

The elastic strain energy density U can be found as follows [15]

$$U = \frac{1}{2}\sigma_{\alpha\beta}\varepsilon_{\alpha\beta}, \tag{11}$$

where the summation is taken over repeated indices.

It simplified Gurtin-Murdoch surface elasticity model is assumed that surface energy depends only on surface strains and does not depend on displacement gradients [18]

$$U_s = \gamma_0(1 + \varepsilon_{tt}^{s}) + \frac{1}{2}(M - \gamma_0)\varepsilon_{tt}^{s}\varepsilon_{tt}^{s}. \tag{12}$$

We seek the components of strain and stress tensors in the first-order approximation of the boundary perturbation technique

$$\sigma_{ij} = \sigma_{ij(0)} + \varepsilon\sigma_{ij(1)},\ \varepsilon_{ij} = \varepsilon_{ij(0)} + \varepsilon\varepsilon_{ij(1)}, \quad (13)$$
$$\sigma^s_{tt} = \sigma^s_{tt(0)} + \varepsilon\sigma^s_{tt(1)},\ \varepsilon^s_{tt} = \varepsilon^s_{tt(0)} + \varepsilon\varepsilon^s_{tt(1)}.$$

At an arbitrary point of the z-plane, the stress components can be expresses through the Goursat-Kolosov complex potentials Φ and Υ [11,19], which are holomorphic, respectively, in the domain B outside of the hole and in the finite region $\tilde{B} = \{z: \bar{z}^{-1} \in \Omega\}$ with the boundary $\tilde{\Gamma}$ symmetrical to the surface Γ relative to the unit circle:

$$\sigma_{nn} + \sigma_{tt} = \sigma_{rr} + \sigma_{\theta\theta} = 2\left[\Phi(z) + \overline{\Phi(z)}\right] = 4\mathrm{Re}[\Phi(z)], \quad (14)$$

$$(\sigma_{tt} - \sigma_{nn} - 2i\sigma_{nt})e^{2i\alpha} = \sigma_{\theta\theta} - \sigma_{rr} - 2i\sigma_{r\theta} = \quad (15)$$
$$= -2\left[\frac{1}{\bar{z}^2}\left(\overline{\Phi(z)} + \Upsilon\left(\frac{1}{\bar{z}}\right)\right) + \left(z - \frac{1}{\bar{z}}\right)\overline{\Phi'(z)}\right]e^{-2i\theta},$$

where α is the angle between the normal vector **n** and the radius vector **r** of the point z, a bar over a symbol denotes the complex conjugation, and a prime denotes the derivative with respect to the argument.

Subtracting Eq. (14) from Eq. (15) passing to the limit for $z \to \zeta$ and taking Eqs. (5) into account, we get the following boundary equation for the definition of the complex potentials Φ and Υ:

$$\sigma_n(\zeta) = \Phi(\zeta) + \overline{\Phi(\zeta)} + \frac{\rho' - i\rho}{\rho' + i\rho}\left[\frac{1}{\bar{\zeta}^2}\left(\overline{\Phi(\zeta)} + \Upsilon\left(\frac{1}{\bar{\zeta}}\right)\right) + \left(\zeta - \frac{1}{\bar{\zeta}}\right)\overline{\Phi'(\zeta)}\right]\bar{s}^2, \quad (16)$$

where $\Phi(\zeta) = \lim_{z\to\zeta} \Phi(z)$ when $z \in B$ and $\Upsilon(\zeta) = \lim_{z\to\zeta} \Upsilon(z)$ when $z \in \tilde{B}$. In accordance with the first-order approximation of boundary perturbation technique [11-13], the unknown functions Φ, Υ and q take the following form

$$\Phi(z) = \Phi_0(z) + \varepsilon\Phi_1(z),\ \Upsilon(z) = \Upsilon_0(z) + \varepsilon\Upsilon_1(z),\ \ q(\zeta) = q_0(\zeta) + \varepsilon q_1(\zeta). \quad (17)$$

Using the approach developed in [13] the solution of the boundary value problem (1)-(6) of plane elasticity is reduced to the successive solution of the hypersingular integral equation in the unknown functions q_n, $n = 0, 1$,

$$[4\mu a - M(\kappa_1 - 1)]q_n(\eta) + \frac{M(\kappa_1+1)}{2\pi i}\int_{|\xi|=1} \frac{\left(\xi + \frac{\eta^2}{\xi}\right)q_n(\xi)}{(\xi-\eta)^2}d\xi = G_n(\eta), |\eta| = 1, \quad (18)$$

where $\kappa_1 = \frac{\lambda+3\mu}{\lambda+\mu}$. The function $G_0 = 0$ and the function G_1 depend on the solution in zero-order approximation.

In this paper, we consider a nanohole the boundary of which is given by the function $\cos 2\theta$. In this case, the surface stress in zero-order and first-order approximation is determined as

$$q_0 = \frac{D_1 M(\kappa_1+1)+\gamma_0}{2\mu a + M},\ \ q_1 = a_{12}\zeta^2,\ \ a_{12} = \frac{M(1.5q_0(1-\kappa_1) - (D_0+D_1)(3+\kappa_1))}{4\mu a + M(\kappa_1+3)}. \quad (19)$$

Here,

$$D_0 = D_1 - q_0,\ \ 2D_1 = \sigma_0. \quad (20)$$

The constants D_0 and D_1 are defined from the conditions at infinity (5). According to the work [13], we obtain the complex potentials in the zero-order and first-order approximation as

$$\Phi_0(z) = D_1,\ \ \Upsilon_0(z) = D_1 - q_0, \quad (21)$$
$$\Phi_1(z) = (\sigma_0 + 0.5q_0 + a_{12})z^{-2},\ \ \Upsilon_1(z) = 3(\sigma_0 - 1.5q_0 - a_{12})z^2.$$

We obtain stress components in an arbitrary point of z-plane from the Eqs. (14), (15), and (21).

Substituting Eqs. (11) and (12) into Eq. (9) taking into account Eqs. (13)-(15) we come to the governing equation describing the dependence perturbation amplitude change on time, bulk and surface elastic parameters, initial radius, diffusion coefficient, and applied stress

$$\ln A(\tau)/A_0 = P(a, \lambda, \mu, \lambda_s, \mu_s, K_s, \sigma_0). \quad (22)$$

4. Numerical results

As an example, we consider a cylindrical pore in an aluminum matrix with bulk parameters $\lambda = 58.17$ GPa and $\mu = 26.13$ GPa. The surface elastic parameters $\lambda_s = 6.851$ N/m and $\mu_s = -0.376$ N/m (i.e., surface stiffness $M = 6.099$ N/m) as well as the residual surface stress $\gamma_0 = 1$ N/m for aluminum with crystallographic orientation (111) were calculated using the molecular dynamic simulations in [20]. Since the surface parameters depend on different factors, we vary surface stiffness and residual surface stress in numerical calculations to analyze the influence of surface elasticity.

Figure 2 shows the perturbation amplitude change as the function of the hole radius a for $\gamma_0 = \{0.5, 1\}$ N/m (blue and red lines, respectively), $M = \{6.099, 60\}$ N/m (solid and dashed lines, respectively), $\sigma_0 = 1$ GPa (a) and $\sigma_0 = 1.5$ GPa (b). The critical radius of the hole is found from the intersection of the lines with the abscissa. If the initial radius of the hole is less than the critical one, the shape of the hole tends to be circular over time.

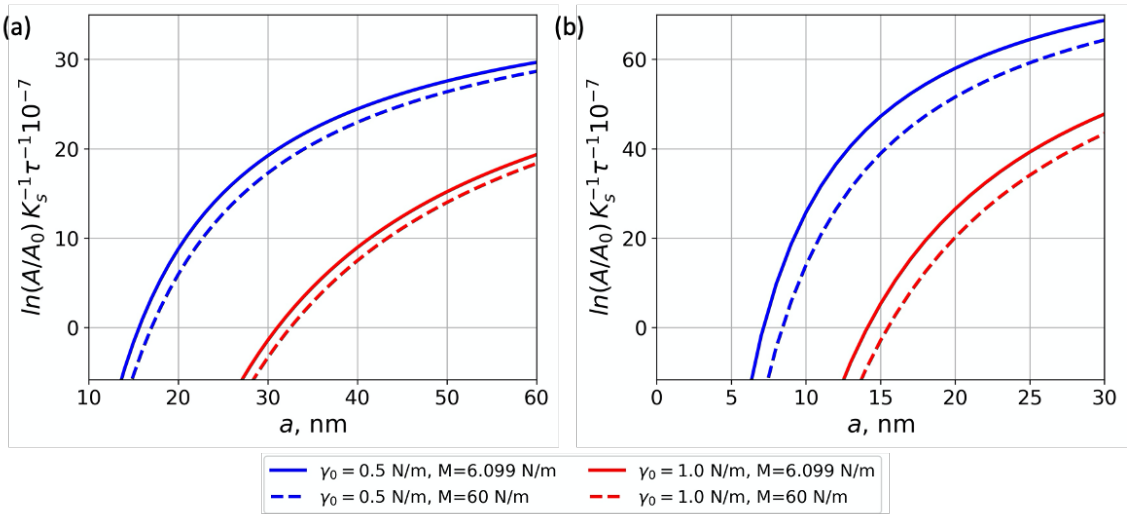

Fig. 2. The dependence of normalized deviation amplitude change $A(\tau)/A_0$ on the initial hole radius a

Figure 3 demonstrate the dependence of the ratio a_{cr}/a_{cr}^0 on surface stiffness M, where a_{cr}^0 correspond to $M = 0$ for $\gamma_0 = \{0.5, 1\}$ N/m (blue and red lines, respectively), $\sigma_0 = 1$ GPa (a) and $\sigma_0 = 1.5$ GPa (b). As one can see from this figure, the critical radius a_{cr} increases with increasing surface stiffness. It is also seen that the impact of surface stiffness increases with decreasing of residual surface stress γ_0 as well as with increasing of applied stress σ_0.

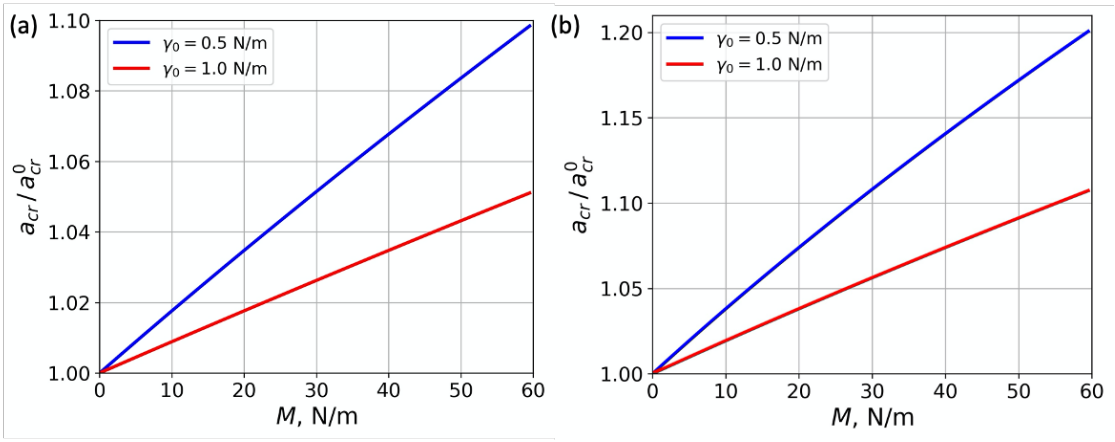

Fig. 3. The influence of surface stiffness M on the critical radius a_{cr}

The influence of residual surface stress γ_0 on critical radius a_{cr} for $M = 6.099$ N/m and $\sigma_0 = \{1, 1.5\}$ GPa (magenta and green lines, respectively) is plotted in Fig. 4. The critical radius a_{cr} increases with the increasing of residual surface stress γ_0.

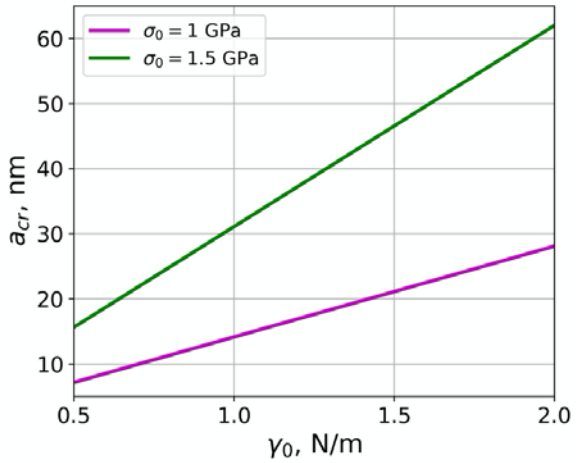

Fig. 4. The dependence of critical hole radius a_{cr} on the residual surface stress γ_0

Note that the change of shape may be observed in solids exposed to loads and aggressive environments. Some problems of uniformly corroded vessels are solved analytically in [21], for local corrosion damage the numerical methods are used [22].

5. Conclusion

The presented paper is devoted to the investigation of the morphology evolution of cylindrical nanopore under diffusion processes. It is assumed that atomic flux along the pore surface is driven by bulk and surface stress fields as well as surface curvature. In order to define stress distribution, the corresponding boundary value problem of plane elasticity has been solved using the asymptotic method described in [13]. Based on the first-order approximation of the boundary perturbation technique we have derived the linearized equation which describes the change of perturbation amplitude with time. A parametric analysis of this equation results in the definition of a critical radius, exceeding which the pore surface is morphologically unstable. The obtained results are summarized as follows:

– the critical pore radius increases with increasing of surface stiffness and residual surface stress as well as with decreasing of applied stress;

– the influence of surface stiffness on morphological stability is increased with increasing applied stress as well as with decreasing of residual surface stress;

– the impact of residual surface stress critical radius is marginally dependent on surface stiffness and tension stress.

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