Electronic Supplementary Material (ESI) for Nanoscale.

Supporting Information

Pore and Ligament Size Control, Thermal Stability and Mechanical Properties of Nanoporous Single Crystals of Gold

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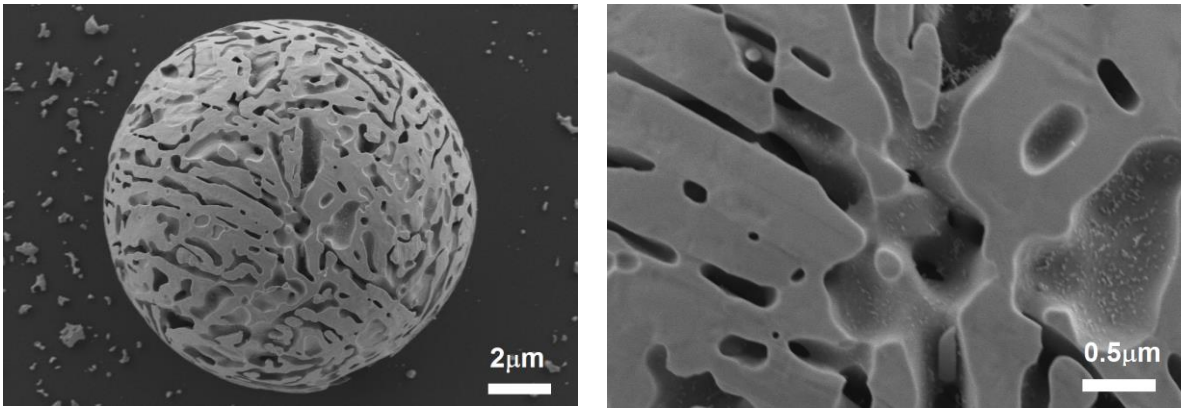
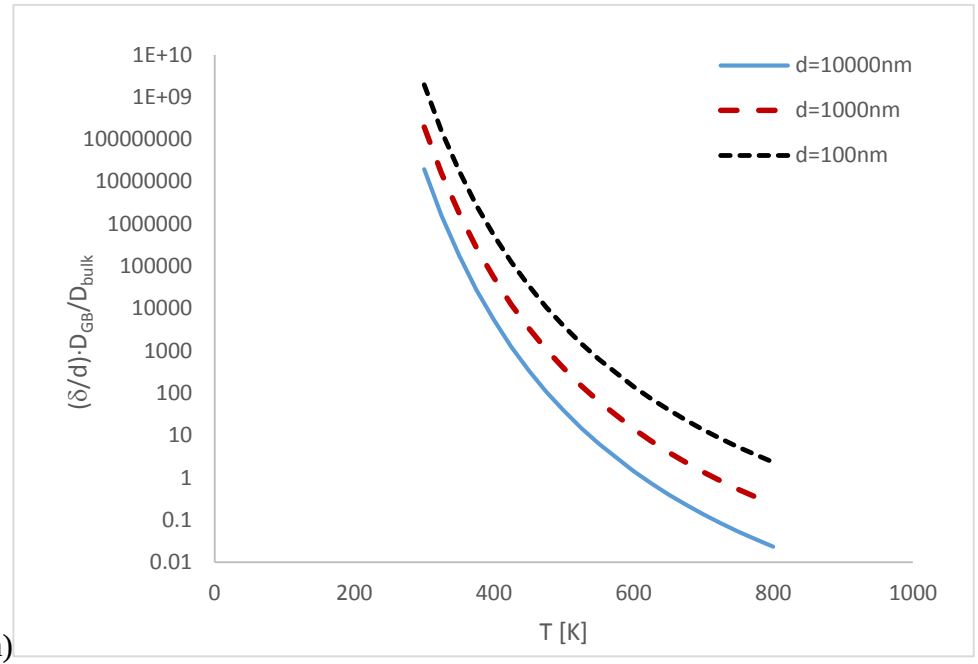
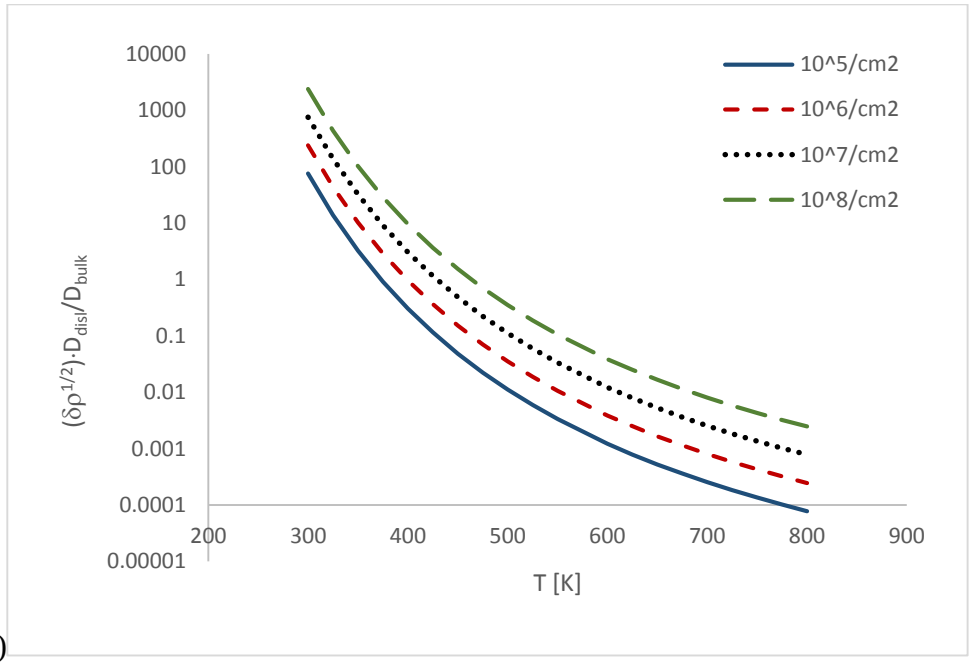


Figure S1. Nanoporous gold particle prepared from sample with 34at% Au. (a) HRSEM image of a gold droplet after wet etching of germanium; top view. (b) HRSEM image of high magnification from (a).



(a)



(b)

Figure S2. (a) The temperature dependence of the ratio of grain boundary to bulk self-diffusion coefficients for different average grain sizes. (b) The temperature dependence of the ratio of dislocation to bulk self-diffusion coefficients for different dislocation densities.

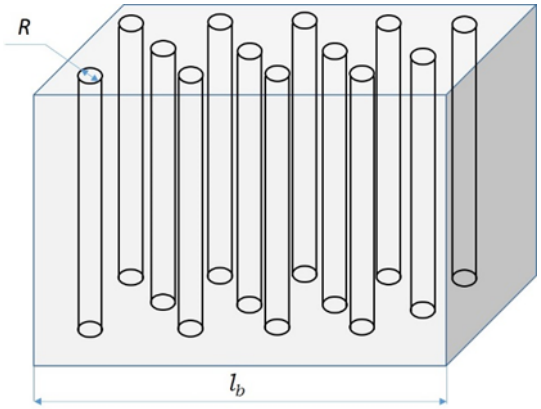


Figure S3. A simplified model of nanoporous material as an array of parallel porous cylindrical channels of a radius R spaced at a distance *l* from each other in real incompressible material.

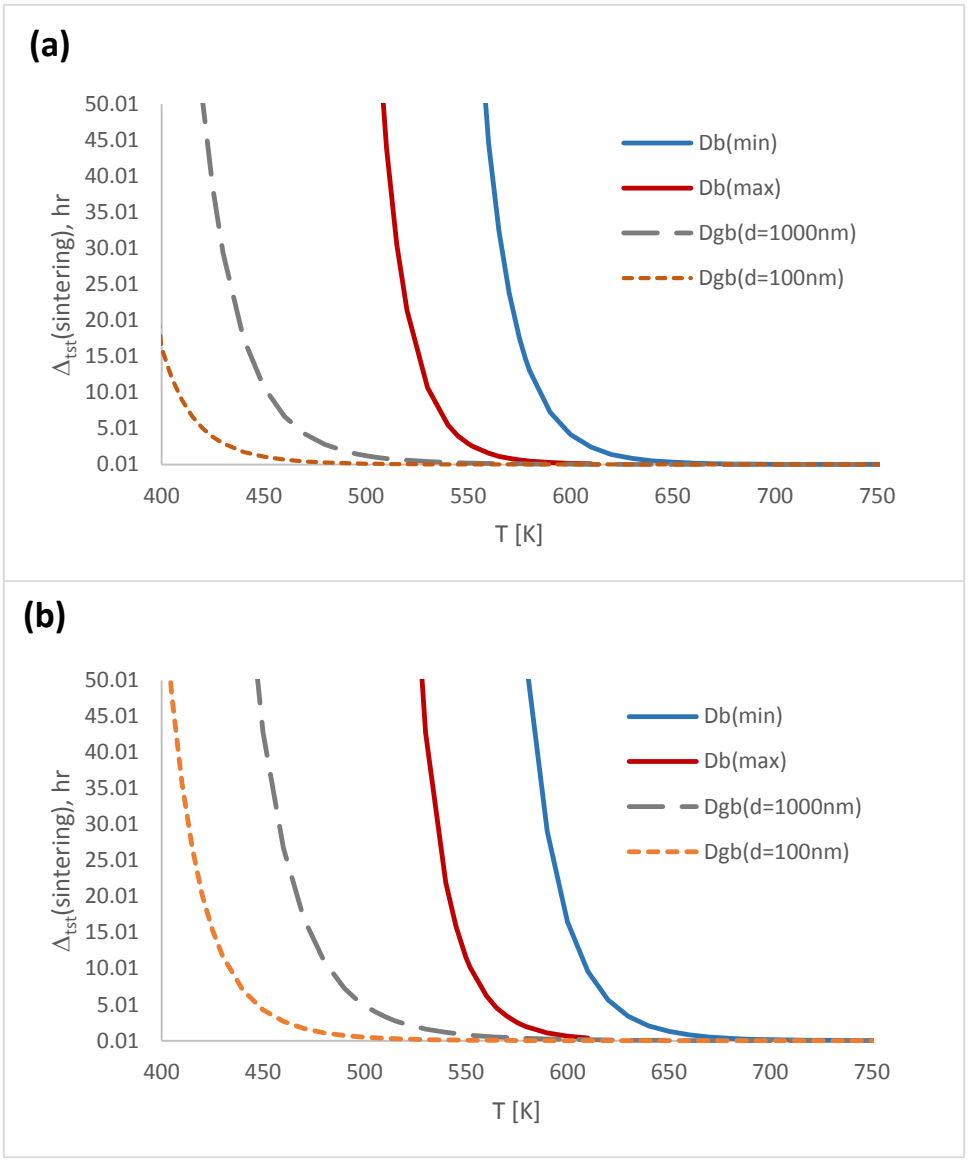


Figure S4. Stability time against sintering of cylindrical-like channels controlled by viscous flow of material under the action of porous surface tension; the bulk diffusion coefficient used $D_m^{min} = 1.1 \exp\left(-\frac{1.77eV}{k_B T}\right) cm^2 s^{-1}$, $D_m^{max} = 6.0 \exp\left(-\frac{1.69eV}{k_B T}\right) cm^2 s^{-1}$; the GB diffusion coefficient: $\delta D_{GB} = 3.1 \cdot 10^{-10} \exp\left(-\frac{0.88eV}{k_B T}\right) cm^3 s^{-1}$. Initial channel radii: R_0 = 25 nm (a) and R_0 = 100 nm (b), γ = 1.28 Jm^{-2}, solid lines – single crystal, dashed lines – polycrystalline material with grain size d = 1 μm or 0.1 μm. D_b is diffusion coefficient of bulk, D_{GB} is grain boundary diffusion coefficient.

Note S1.

The Ligament Size in Hypereutectic Au-Ge alloys.

The ligament size of eutectic structure depends on the undercooling reached during eutectic solidification. The process limiting the solidification start is nucleation of a first eutectic two-phase nucleus. In the case of hypoeutectic composition the slowest process is heterogeneous nucleation of Ge crystal nuclei, since Au crystal grows as continuation of existent single gold crystal.[1] In the case of hypereutectic composition (excess of Ge) the limiting rate process is heterogeneous nucleation of Au crystals at liquid/solid Ge interface. As we know from previous investigation, the first nucleated gold crystal, together with growing Ge crystals form the eutectic structure consisting of one single gold crystal and rod-like Ge crystals. The growth rate of this structure is about 10÷30 μms^{-1},[2] and thus the undercooling reached after nucleation of first nucleus is almost constant during solidification of micron-sized droplets.

Probability of heterogeneous Au nucleation per unit time ϕ is proportional to a surface of the liquid/Ge interface S and therefore $\phi = kS$, where k is the proportionality coefficient. For round shape of Ge solid particles, this surface S is proportional to $f^{2/3}$, where f is the volume fraction of the solid germanium phase:

$$f = \frac{X_{Ge} - X_{Ge}^{eut}}{1 - X_{Ge}^{eut}}, \tag{1S}$$

where X_{Ge} is the total concentration of Ge in the alloy, X_{Ge}^{eut} is the eutectic concentration of Ge. In order to evaluate the influence of total germanium concentration on the final ligament size of eutectic structure, let us assume that the time needed for heterogeneous nucleation of a first gold crystal is inversely proportional to the surface S (since $\Delta t \cdot \phi = \Delta t \cdot kS = 1$):

$$\Delta t \sim S^{-1} \sim f^{-2/3} \tag{2S}$$

Then, the undercooling ΔT, reached during cooling with the rate α, $\Delta T = \alpha \Delta t$, is also proportional to $f^{-2/3}$. According to theory of eutectic solidification of Turnbull,[3,4] the ligament size λ is inversely proportional to the undercooling:

$$\lambda = 2\lambda^* = \frac{4\gamma_{\alpha\beta} v_{mol}}{\Delta T \Delta S_{tr}} \tag{3S}$$

where $\gamma_{\alpha\beta}$ is the energy of the solid/solid (Au/Ge) interface, v_{mol} is the liquid molar volume, ΔS_{tr} is the entropy change in the L (eutectic) $\rightarrow$ Au(s) + Ge(s) transformation. Using the transformation entropy value for the Au-Ge system[5] ΔS_{tr} = 23.9 $Jmol^{-1} \cdot K^{-1}$, $\gamma_{\alpha\beta}$ = (0.2÷0.4) Jm^{-2} and $v_{mol} = 10^{-5} m^3$ one can find that the ligament size 70 nm corresponds to undercooling

$\Delta T_1 = (5 \div 10) K$, while the ligament size 220nm corresponds to $\Delta T_2 = (1.6 \div 3.8) K$. Using Equations (1S)-(3S), one can write:

$$\frac{\lambda_2}{\lambda_1} = \frac{\Delta T_1}{\Delta T_2} = \left(\frac{X_{Ge,2} - X_{Ge}^{eut}}{X_{Ge,1} - X_{Ge}^{eut}} \right)^{2/3} \quad (4S)$$

For two investigated alloys, $X_{Ge,1} = 0.33 \pm 0.01$ and $X_{Ge,2} = 0.52 \pm 0.01$. Using $X_{Ge}^{eut} = 0.28$ one can obtain $\lambda_2 / \lambda_1 = 2.4 \div 3.4$, which is reasnably close to the experimental ratio of ligament sizes in these two alloys, ~3.1 (see table 1). The higher concentration of Ge $X_{Ge,3} = 0.66 \pm 0.01$ should result in the ratio $\lambda_3 / \lambda_1 = 3.9 \div 4.6$ with the ligament size 270÷320 nm. However, the experimental values of ligament size for this sample vary significantly throughout the droplet around 500 nm (Figure S1), the behavior which is beyond the scope of this study.

Therefore, the presence of larger amount of solid germanium phase before eutectic solidification results in smaller undercooling realizing during eutectic structure growth. That is why the larger total (hypereutectic) Ge concentration results in the larger ligament size of the eutectic structure.

Note S2.

The Rate of Sintering of Cylindrical Porous Material

Following to the approach of Mackenzie and Shuttleworth[6] it is assumed that deformation during sintering is due to surface tension and that the porous material has homogeneous mechanical properties defined by an equation of state connecting the rate of shear strain with the shear stress. The material will also be assumed to be incompressible. In order to simplify the calculations, we consider a special model (Figure S2) in which all the pores are isolated equal cylindrical channels distributed at equal distance, *l*, from each other in the real solid material.

Further approximation consists in replacing the material outside the cylindrical shell by the equivalent homogeneous material, in which a channel of radius R_1 is surrounded by a cylindrical shell of the real incompressible material, out to some radius R_2, and then by homogeneous continuum with the relative density, ρ:

$$\rho = 1 - R_1^2 / R_2^2 = 1 - \theta \tag{5S}$$

where $\theta = R_1^2 / R_2^2$ is the porosity; the condition that the channel and its shell have the same density as the array of channels is $R_2 = l\sqrt{\pi}$.

The problem is now reduced to the calculation of the rate of decrease in radius R_1 of the channel, surrounded by a shell of incompressible but shearable material, when a Laplacian pressure $-\gamma / R_1$ is applied inside the channel, γ is the surface tension. Because the material is supposed incompressible, the effect of surface tension in closing the pores is equivalent to the application of an external pressure $+\gamma / R_1$ to the surface of the compact.[6]

If the rate of cylindrical radial strain is $\dot{\varepsilon}$, the condition of incompressibility shows that the rate of strain in the direction perpendicular to the cylinder axis is $-\dot{\varepsilon}$ and zero in the direction parallel to this axis. The rate of the channel closing is calculated by equating the energy dissipated by the flow of the material in the shell to the work done by the surface tension:

$$\frac{dW_s}{dt} = \frac{dW_0}{dt} \tag{6S}$$

The work done by the surface tension per unit time:

$$\frac{dW_s}{dt} = -\frac{d}{dt}\left(2\pi RL\gamma\right) = -2\pi L\gamma u_R \tag{7S}$$

where $u_R = dR / dt$ is the radial velocity of the channel surface. The rate of energy dissipation per unit volume for the case of cylindrical symmetry can be found from the theory of' viscosity

as given, for example, by Lamb,[7] $\dot{E} = 4\dot{\varepsilon}^2\eta$, and the energy dissipated throughout the whole volume of the shell:

$$\frac{dW_0}{dt} = 4\int_R^{R_0} \dot{\varepsilon}^2\eta(\dot{\varepsilon})dV = 8\pi L\int_R^{R_0} \dot{\varepsilon}^2\eta(\dot{\varepsilon})rdr \qquad (8S)$$

Now, since the real material is incompressible, the radial velocity at any cylindrical radius is inversely proportional to the radius. Thus, $u_r = u_R \cdot (R/r)$ and $\dot{\varepsilon} = \frac{du_r}{dr} = -u_R \frac{R}{r^2}$. Assuming a solid which has a Newtonian viscosity, η is independent of the rate of strain, from Equations (6S)-(8S) one can obtain:

$$u_R = -\frac{\gamma}{2\eta}\frac{1}{\rho} \qquad (9S)$$

The volume of real material in the porous compact does not change. One can assume that also the total number of channels does not change during initial stage of annealing.

Let us obtain a relation between the relative density and the time of sintering. The total area of pores per unit area perpendicular to the channel axis is $\pi R^2 n = (1-\rho)/\rho$ and therefore:

$R = \left[(1-\rho)/\pi n\rho\right]^{1/2}$. Since $u_R = dR/dt$, from Equation (9S) one can obtain:

$$\frac{d\rho}{dt} = \frac{\gamma}{2\eta}\left[\pi n\rho(1-\rho)\right]^{1/2} \qquad (10S)$$

After integration the time of sintering is obtained as a function of final density ρ:

$$\frac{\gamma}{2\eta}(\pi n)^{1/2}(t-t_0) = \int_{\rho_0}^{\rho} \frac{d\rho}{\rho^{1/2}(1-\rho)^{1/2}} = 2\left(arcsin\sqrt{\rho} - arcsin\sqrt{\rho_0}\right) \qquad (11S)$$

The time t_0, from which the sintering is measured, is determined by the initial density ρ_0. In the considered case of porous gold, $\rho_0 \approx 0.7$ and $arcsin\sqrt{\rho_0} \approx 1$.

The time of full sintering ($\rho = 1$) can be estimated as

$$\Delta t_s = (t_f - t_0) = \frac{2\eta}{\gamma}\left(\frac{\pi - 2}{n}\right)^{1/2} \qquad (12S)$$

Using the usual expression for viscosity: $\eta = l_b^2 kT / D_{eff}\Omega$, where l_b is the characteristic size of microstructure, one can obtain Equation 2 presented in the main text of the paper.

References:

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