Inverse Hall–Petch relationship in the nanostructured TiO$_2$: Skin-depth energy pinning versus surface preferential melting

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The functional dependence of stress, elastic modulus, melting point, and their interdependence on the identities (bond order, nature, length, and strength) of a representative bond of the specimen has been established for deeper insight into the transition from the conventional Hall–Petch relationship (HPR) to the inverse HPR (IHPR) for nanostructured TiO$_2$. Theoretical reproduction of the observed inverse HPR suggests that the intrinsic competition between the energy-density gain (elastic modulus enhancement) and the cohesive-energy remnant (melting point depression) in the grain boundaries originates and the extrinsic competition between the activation and the inhibition of atomic dislocations activates the IHPR. © 2010 American Institute of Physics. [doi:10.1063/1.3471818]

I. INTRODUCTION

Intensive investigations,$^{1-4}$ revealed that the Young’s modulus ($Y$) of TiO$_2$ nanostructures increases with the inverse of the feature size and that the hardness (or stress, $P$) of TiO$_2$ at the submicrometer scale follows the classical $T$-independent Hall–Petch relationship (HPR). However, with further reduction in the solid size down to 20 nm or so, the HPR process invariably breaks down and the $P$ descends.$^{5-8}$ This phenomenon has been termed as the inverse HPR (IHPR).$^{3-13}$ The HPR can be simplified in a dimensionless form that is normalized to the bulk strength, $P(0,T)$, measured at the same temperature and under the same conditions as follows:

$$P(x,T)/P(0,T) = 1 + A x,$$  \hspace{1cm} (1)

where the slope $A$ is an adjustable parameter used to fit the experimental result, $x = K^{-1/2}$, and $K$ is the number of atoms lined along the radius of the spherical or cylindrical specimens or across the thickness of a thin film. This HPR reflects the extrinsic factors such as shapes of indentation tips and the intrinsic properties such as impurities and defects.

Despite the existing models such as dislocation,$^{6,14}$ diffusion,$^{15}$ grain-boundary-shearing,$^{16}$ core-shell-role-exchange,$^{17}$ two-phase structures,$^{18}$ collective-dislocation,$^{19}$ dislocation-absorption models,$^{20}$ and so on at the grain boundaries, the atomistic origin of the IHPR transition and the paradox between the elastic modulus and the stress remain yet unclear. Recently, we have addressed this issue in terms of local bond average (LBA) approach. By establishing the functional dependence of the detectable quantities of a specimen on the bond nature, bond order, bond length, and bond energy and their response to the temperature and pressure change using the core-shell configuration, we have been able to reproduce the size trends of some properties for nanostructures.$^{7,12,22}$ Due to the limitation of available database, we have been unable to show the consistency between theory and measurements of the size dependence of the elastic modulus, melting point, and the mechanical stress of a particular specimen. The well-measured and calculated data$^{1,4,5,23}$ for TiO$_2$ has enabled thus as reported herewith. In order to demonstrate the interdependence and the size dependence of these quantities, this work focuses on the nanostructured TiO$_2$ by incorporating the bond order-length-strength (BOLS) correlation theory,$^{22,24}$ LBA approach,$^{22}$ and the conventional HPR premise$^{2,3}$ to present deeper insight into the unusual mechanical behavior of TiO$_2$ at the nanoscale. Theoretical reproduction of the observed trends confirms that the transition from the HPR to the IHPR originates from the intrinsic competition between the energy-density gain (or elastic enhancement$^{25}$) in the surface skin up to three atomic layers and the cohesive-energy depression ($T_m$ suppression$^{24}$) of the under-coordinated surface atoms. The extrinsic competition between activation and inhibition of atomic dislocations associated with the contacting measurement activates the IHPR.

II. PRINCIPLES

According to Goldschmidt–Paulings’ rule of bond contraction$^{26,27}$ and the BOLS correlation theory, the bonds between under-coordinated atoms contract from the bulk value of $d_0$ to $d_i = c_i d_0$ and the cohesive energy per bond increases from the bulk value of $E_b$ to $E_i = c_i^{m} E_b$, where $c_i$ is...
the Goldschmidt–Pauling bond contraction coefficient that varies only with the effective coordination number (CN or $z_i$) of an atom of concern, regardless of the nature of the bond.23,24 The index $m$ is the bond nature indicator that is not freely adjustable for a given material. The subscripts $i$ and $b$ denote an atom in the $i$th atomic layer and in the bulk, respectively. The $i$ is counted from the outermost atomic layer up to three inward, as no bond-order loss occurs for $i$ bond.22,24 The index of an atom of concern, regardless of the nature of the

$$P_i \propto B_i$$

where the linear thermal expansion coefficient is in the range $(T_m)$ to the atomic cohesive energy ($E_i$) per discrete atom (in the units of electron volt per atom) that equals to the multiplication of the bond energy ($E_i$) and the atomic CN:24

$$E_i = \frac{\partial^2 u(r)}{\partial V^2} \propto \frac{E_i(d_i)}{d_i^3}; \quad P_i = -\frac{\partial u(r)}{\partial V}$$

It has been clear that the local elastic modulus $Y_i$ and stress $P_i$ at the $i$th atomic site are proportional to the binding energy density (in the units of electron volt per cubic meter) (Ref. 30) and the melting temperature ($T_m$) to the atomic cohesive energy ($E_i$) per discrete atom (in the units of electron volt per atom) that equals to the multiplication of the bond energy ($E_i$) and the atomic CN:24

$$T_m \propto z_iE_i,$$

where $u = u(r)$ is the interatomic potential. It can readily be shown that both quantities are in the same dimension (pascal) in the elastic regime for $B$ ($r=d$, $Y \sim 3B$) and plastic regime ($r \neq d$) for $P$, respectively.

Therefore, the mechanical strength is connected to the bond nature, order, length, and strength ($m$, $z_i$, $d_i$, $E_i$), which can be expressed in terms of the BOLS coefficients in the following:

$$Y(z_i, T) = Y(z_b, T_0) \times \frac{P(z_i, T)}{P(z_b, T_0)} \times \frac{E(z_i, T)}{E(z_b, T_0)} \times \frac{d(z_i, T)}{d(z_b, T_0)} \times \frac{T_m(z_i, T)}{T_m(z_b, T_0)} = \eta_1(T_m, T) = \frac{E_i(z_i, T)}{E_i(z_b, T_0)} \times \frac{d_i(z_i, T)}{d_i(z_b, T_0)} \times \frac{T_m(z_i, T)}{T_m(z_b, T_0)}$$

where the linear thermal expansion coefficient is in the range of $\alpha(T_m) = 2 - 4 \times 10^{-7}/T_m$, which can be neglected in numerical calculations compared to the extent of size-induced bond contraction that is in the order of 10%. The $\eta_1$ is the specific heat per bond and $\theta_D$ is the Debye temperature. The $\eta_2$ is 1/$z_i$ fold of the latent heat of atomization for the $i$th atom from the molten state. The term of $\eta_1(T_m, T)$, being a fraction of the bond energy in the bulk ($E_b$), is also 1/$z_i$ fold thermal energy required for thermally dissolving the specific atom from the bulk at the current temperature $T$.

Combining Eqs. (2) and (3), we can readily obtain the $T$-dependent $Y(z_i, T)$ and $P(z_i, T)$ at the $i$th atomic site with respect to the corresponding known bulk values as follows:

$$\left\{ \begin{align*}
    c_i &= d_i/d_0 = 2/[1 + \exp[(12 - z_i)/(8z_i)]] \\
    c_i^{-m} &= E_i/E_b \\
    c_i^{-(m+3)} &= E_{id}/E_{ddb} \propto Y_i/Y_b \propto P_i/P_b \\
    z_iE_i^{m} &= E_i/c_i^{m} \propto T_m/T_{mb} \\
    \end{align*} \right. \quad (T \ll T_m)

(2) \quad \begin{align*}
    d_i(z_i, T) &= d_b(z, T_0) \times C_i \times \left(1 + \int_0^T \alpha(t) dt\right) = d_bC_i(1 + \alpha T) \\
    E_i(z_i, T) &= E_b(z, T_0) \times C_i^{m} - \int_0^T \eta_1(t) dt = \eta_2i + \eta_1(T_m, T) \\
    \end{align*}

$$\eta_1(T_m, T) = \frac{\eta_1(T_m, T)}{T_m}$$

(3)
where the constant $\eta_{21} = \eta_{2b}/\eta_{1b}$ is taken as the zero reference for the contacting measurement as during the transition from the molten to the gaseous phase, the hardness of a material is negligibly small; otherwise, a small offset could exist, which is hardly detectable in the predicted relative changes.\textsuperscript{24} Equation (4) indicates that an increase in $T$ or a decrease in $T_m$ will lower the mechanical strength of the bond. Therefore, the separation $T_m-T$ is crucial to the mechanical strength of the specific bond. It is necessary to mention the operating temperature when we discuss the mechanical strength of a material. Factors that dominate the local mechanical strength of the specific bond, specific heat, bond strain, and effective CN, which determines the size trend.\textsuperscript{2,3} Temperature dependent HPR as follows:

\begin{equation}
\begin{align*}
\frac{\Delta d(x)}{d(\infty)} &= \sum_{i\leq 3} \gamma_i(c_i - 1) = \frac{\tau}{K} \sum_{i\leq 3} c_i(c_i - 1) = \Delta_x x^2 \\
\frac{\Delta T_m(x)}{T_m(\infty)} &= \sum_{i\leq 3} \gamma_i(z_i c_i^{-2} - 1) = \frac{\tau}{K} \sum_{i\leq 3} c_i(z_i c_i^{-2} - 1) = \Delta_{T_m} x^2 \\
\frac{\Delta Y(x)}{Y(\infty)} &= \sum_{i\leq 3} \gamma_i(c_i^{-(m+3)} - 1) = \frac{\tau}{K} \sum_{i\leq 3} c_i(c_i^{-(m+3)} - 1) = \Delta_{Y_m} x^2,
\end{align*}
\end{equation}

where $\gamma_i = \pi c_i/K = \pi c_i x^2$ is the surface-to-volume ratio representing the geometrical contribution from size, dimensionality, and effective CN, which determines the size trend. $\tau = 1$, $2$, and $3$ corresponds to a thin plate, cylindrical rod, and spherical dot, respectively. It has been shown\textsuperscript{30} that any size trends are dictated by atoms in the surface skin of limited number of atomic layers while atoms in the core interior make no contribution.

Substituting the size dependent $\eta_1(x)$, $d(x)$, and $T_m(x,m)$ for the $\eta_{1r}$, $d_r$, and $T_{mr}$ in Eq. (4), the size and temperature dependence of the mechanical strength of a nanosolid can be obtained as follows:

\begin{equation}
P(x,T) = \eta_1(x) \left[ \frac{d(0)}{d(x)} \right]^3 \frac{T_m(x,m) - T}{T_m(0) - T} = \frac{P(x)}{P(0)} f(d,m,T).
\end{equation}

The additional term $f(d,m,T)$ includes contributions from the bond nature, specific heat, bond strain, $T_m$ suppression, and temperature of operation $T$, to the mechanical strength of a solid. Equating Eq. (6) at $T=0$ to the traditional $T$-dependent HPR given in Eq. (1), one can find that the ratio of the specific heat per bond follows the relation of $\eta_1(x)/\eta_1(0) = P(x,T)/P(0,T) = 1 + A x$. Incorporating the activation energy for atomic dislocation, $E_a \times T_m$,\textsuperscript{8,12,31} into the prefactor $A$ leads to an analytical expression for the size and temperature dependent HPR as follows:

\begin{equation}
Y(x,T) = \frac{P(x,T)}{P(0,T)} \frac{\eta_1(x)}{\eta_1(0)} \left[ \frac{d(0)}{d(x)} \right]^3 \frac{1 + \Delta_{T_m} x^2}{1 - \theta(T)}.
\end{equation}

Generally, the effective CN, $z_r$, varies with the size of a nanostructure in the form of $z_1 = 4(1 - 0.75/K)$, $z_2 = z_1 + 2$, and $z_3 = 12$, where the $K$ is the number of atoms lined along the radius of a sphere or across the thickness of a thin film.\textsuperscript{24} As a result, local strain, energy-density gain, and atomic cohesive-energy loss take place simultaneously in the relaxed grain boundaries of a nanostructure whereas atoms in the core interior remain in their bulk nature.\textsuperscript{24} Taking the contributions of the shorter and stronger bonds between under-coordinated boundary atoms into consideration, the size dependent $d(x)$, $T_m(x)$, and $Y(x)$ of a nanosolid at constant temperature can be obtained by an average of the core-shell structural configuration as follows:

\begin{equation}
Y(x,T) = \frac{P(x,T)}{P(0,T)} \frac{\eta_1(x)}{\eta_1(0)} \left[ \frac{d(0)}{d(x)} \right]^3 \frac{T_m(x) - T}{T_m(0) - T} = \frac{1 + A[x, \theta(x), m]}{T_m(0) - T} \times \frac{1 + \Delta_{T_m} x^2}{1 - \theta(T)}.
\end{equation}

where $A[x, \theta(x), m] = f \times x \times \exp[\{T_m(x)/T_m(0)\}] = f \times x \times \exp[\{1 + \Delta_{T_m} x^2/\theta(T)\}]$ and $\theta(T) = T/T_m(0)$. The prefactor $f$ is adjustable under the constraint that the slope of the traditional HPR should match the observations and the intercept must be at the positive side of the vertical axis of the $P$-$x$ curve. The $f$ should represent the contribution from extrinsic factors such as the purity or defect density, shape of tips, and loading scales to the mechanical strength of a solid. When the $x$ approaches zero or $K$ is infinitely large, the analytical form degenerates into the traditional HPR in which the slope is clarified herewith to be dominated by the term $f \times \exp[\{T_m(0)/T\}]$ that relates to the specific heat or activation term for atomic dislocation.

\section{RESULTS AND DISCUSSION}

By combining Eqs. (2) and (5), we can calculate the size dependence of $T_m(x)$ and $Y(x)$. By matching the predicted $T_m(x)$ and $Y(x)$ to the measured data, we can also obtain the $m$ value that is unique for a given material. Figures 1(a) and
Figure 1. Theoretical reproduction of the reported size dependence of (a) the Young’s modulus $Y$ for TiO$_2$ nanowires (Ref. 1) in dealing with numerically the tensile behavior of TiO$_2$ nanowires using molecular dynamic simulations and (b) the $T_m$ for TiO$_2$ nanowires and nanoparticles (Ref. 23) using thermodynamics approach with the derived mean $m = 5.34$ for TiO$_2$ nanostructures.

1(b) present the theoretical reproduction of the reported size dependence of the $Y$ for TiO$_2$ nanowires$^1$ and the $T_m$ for TiO$_2$ nanowires and nanoparticles$^{23}$ with the optimal mean $m$ value of 5.34, respectively. The agreement confirms the occurrence of surface energy densification and atomic cohesive-energy depression. The predicted $Y$ enhancement agrees with the measured trend of ZnO nanostructures$^{30}$ and the size dependent strain and elastic modulus of Ni, Cu, and Ag nanostructures$^{22,32}$ without showing the IHPR trend. The predicted size dependence of $T_m$ depression also agrees with the measured size dependence for many kinds of nanoparticles. Furthermore, the results indicate that when the feature size is reduced, the elastic modulus rises while the melting point decreases, which confirms that the broken-bond-induced binding energy-density gain and atomic cohesive-energy depression in the surface up to skin depth.

In the IHPR calculation, the standard bulk values of $d_0 = 0.386$ nm, $T_m = 2098$ K, $T_p = 300$ K, and the derived mean $m$ value are taken as input. The theoretical curves are normalized according to the calculated peak values at $x_C$, and the experimental data measured at room temperature are normalized to the measured maximum $P_m$. Figure 2 shows the theoretical reproduction of the experimentally and computationally observed IHPR for TiO$_2$ nanoparticles.$^{4,5}$ The straight line is the traditional $T$-independent HPR and the slope is obtained by adjusting the $f$ values in Eq. (7). For TiO$_2$, the $f$ value is 0.01 for the corresponding HPR. A slight discrepancy in the critical size and the disparity at the smaller size $x > 0.3$ may arise from experimental conditions or other factors such as size distribution and impurities that are represented by the factor $f$. Nevertheless, the predicted and the measured trends of change match fairly. Reproduction of the measured data in trend implies the following.

(i) The IHPR originates intrinsically from the broken-bond-induced lattice strain, energy-density gain, and cohesive-energy loss in the surface skin of nanostructures, which can be activated by plastic deformation.

(ii) The measurable IHPR is dominated by the competition between the energy-density ($\approx Y$) gain and surface preferential melting ($[T_m - T] < [T_{mb} - T]$). The energy-density gain in the surface skin and the effect of strain work hardening are responsible for the inhibition of atomic dislocations, and yet the cohesive-energy loss caused by the under-coordinated grain boundary atoms dominates the dislocation activation.

(iii) When the grain is greater than the strongest size at the turning point of the IHPR, the process of dislocation inhibition is dominant. At the strongest size, the processes of activation and inhibition of dislocations contribute competitively and during softening, contribution from the cohesive-energy loss becomes dominant.

It is interesting to note that for the same materials, the size trends of $Y$ and $P$ at the nanoscale are different. The $P$ measurement via contact mode in the plastic deformation reveals IHPR but the $Y$ measurement at the elastic regime does not. The $Y$ represents the elastic deformation in the vicinity of structural equilibrium while the $P$ the plastic deformation. Therefore, the activation and annihilation of dislocations is the key to triggering the IHPR.

Current understanding supports Luo$^{33,34}$ who first proposed the concept of subsolidus liquid-like interface complex for the stabilization of nanoscale surface amorphous films for Bi$_2$O$_3$ on ZnO, VO$_x$ on TiO$_2$, SiO$_2$ on Si, and so on. They demonstrated the grain boundary interface prewetting phenomena with analogy to water and other simple systems as well as stabilization of intergranular amorphous films in ceramics. Experimental results show that in the subeutectic regime, the equilibrium film thickness decreases monotonically with decreasing temperature until it vanishes at a dewetting (preshutting) temperature. With increasing temperature, the nanometer-thick interface persists into a solid-liquid coexistence regime in equilibrium with partial-wetting drops
showing a gradual decrease in the macroscopic contact angle upon heating. These solidus interfaces are alternatively considered to be disordered multilayer adsorbates formed from coupled prewetting and premelting transitions.

IV. CONCLUSION

In summary, an analytical solution to the mechanical strength and its correlation to the melting point and elastic modulus of TiO₂ nanostructures has been presented by a combination of the BOLS correlation, the LBA approach, and the conventional HPR for the understanding the atomistic origin of the IHPR. Agreement between predictions and the conventional HPR for the understanding the atomistic origin of the IHPR and to identify the factors dominating the strongest sizes in nanostructured materials.

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