FACTORS CONTROLLING THE STRONGEST SIZES IN THE INVERSE HALL–PETCH RELATIONSHIP

YONG PAN∗, ZHAO FENG ZHOU∗, SHAO-YUN FU†,‡,§, YANGUANG NIE‡ and CHANG Q. SUN‡,¶

∗Key Laboratory of Low-Dimensional Materials and Application Technologies, Xiangtan University
Ministry of Education, Hunan 411105, P. R. China
†Institute of Physics and Chemistry
Chinese Academy of Sciences, Beijing 100190, P. R. China
‡School of Electrical and Electronic Engineering
Nanyang Technological University, Singapore 639798
§syfu@mail.ipc.ac.cn
¶ecqsun@ntu.edu.sg

Received 27 April 2008

Incorporating the bond–order–length–strength correlation mechanism [C. Q. Sun, Prog. Solid State Chem. 35, 1 (2007)] and Born’s criterion for melting [J. Chem. Phys. 7, 591 (1939)] into the conventional Hall–Petch relationship has turned out an analytical expression for the size and temperature dependence of the mechanical strength of nanograins, known as the inverse Hall–Petch relationship (IHPR). Reproduction of the measured IHPR of Ni, NiP, and TiO₂ nanocrystals revealed that: (i) the competition between the size-induced energy–density gain and atomic cohesive energy loss in the surface skins of nanograins originate from the IHPR; (ii) the competition between the activation and inhibition of atomic dislocations motion activates the entire IHPR behavior; (iii) the bond nature involved and the \( \frac{T}{T_m} \) ratio between the temperature of operating and the temperature of melting dictate the measured strongest sizes of a given specimen; (iv) a quasimolten phase present before melting determines the size-induced softening and the superplasticity of nanostructures.

Keywords: Hall–Petch effect; nanostructures; nanomechanics; chemical bond; mechanical failure.

PACS Nos.: 62.25.-g, 85.35.Be, 05.45.Ac.

1. Introduction

The mechanically strengthening with grain refinement in the size range of sub-micrometers has traditionally been rationalized with the conventional temperature-independent Hall–Petch relationship (HPR) that can be simplified into a dimensionless form being normalized by the bulk standard, \( P(0) \), or the flow stress, measured under the same conditions,

\[
P(x) = 1 + Ax, \quad (1)
\]

where the slope \( A \) is an adjustable parameter used to fit experimental data. \( K = R/d \) and \( x = K^{-1/2} \) are the dimensionless forms of size, which correspond to the number of atoms, with mean

\[
175
diameter $d$, lined along the radius, $R$, of a spherical-like nanograin, as illustrated in Fig. 1. Using the dimensionless form of the mechanical strength and the grain size in Eq. (1), the study aims to minimize the contribution from artifacts such as the processing conditions and the crystal orientation. The HPR has been well understood in terms of the pile up of dislocations that resist plastic flow from grain refinement.\(^2,^3\)

However, as the crystal is refined from the micrometer regime into the nanometer scale, the HPR process invariably breaks down, and the relationship of yield strength versus grain size departs markedly from that seen at larger grain sizes. With further grain refinement, the maximal yield strength, in many cases, peaks at a mean grain size in the order of 10 nm or so. A further decrease in grain size can cause softening of the solid instead, and then the HPR slope turns from positive to negative at a critical size, or the so-called strongest size. The deviation from HPR is called the inverse Hall-Petch relationship (IHPR).\(^4^-^9\)

There is a concerted global effort underway toward deeper insight into the IHPR mechanism with postulated explanations in terms of dislocation-based,\(^10\) diffusion-based,\(^11,^12\) grain-boundary-shearing-based,\(^13\) core-shell-role-exchange-based,\(^14\) two-phase-based,\(^15\) collective-dislocation-based,\(^16\) and dislocation-absorption-based\(^17\) models. It has been suggested that the grain boundaries (GBs) consisting of under-coordinated atoms contribute to the GB performance.\(^18\) The strongest Cu grain size of 10–15 nm, for instance, is attributed to a switch in the microscopic deformation mechanism from dislocation-mediated plasticity in the coarse-grain interior to the GB sliding in the nanocrystalline regime.\(^19\) A significant portion of atoms resides in the GB, and the plastic flow of the GB region is responsible for the unique characteristics displayed by such materials.\(^20\) In the HPR regime, crystallographic slips in the grain interiors govern the plastic behavior of the polycrystallite, while in the IHPR regime, GB dominates the plastic behavior. During the transition, both grain interior and GB contribute competitively. The slope in the HPR is suggested to be proportional to the work required to eject dislocations from GBs.\(^21\) The strongest size is suggested to depend strongly on the stacking-fault energy and the magnitude of the applied stress.\(^22,^23\) Unfortunately, few reports are available on theoretical reproduction of the observed IHPR, based on the proposed perspectives.

Although there is a growing body of experimental evidence for such an unusual deformation in the nanometer regime, the underlying atomistic mechanisms for IHPR are yet poorly understood, which seems beyond the scopes of the classical continuum mechanics or classical thermodynamics or the quantum mechanical computations. As pointed out by Kumar et al.\(^24\) and Mayrhofer et al.\(^25\) the physical origin of the IHPR transition and the factors dominating the strongest size have been a long-standing puzzle. The objective of this contribution is to show that a combination of the conventional HPR,\(^1\) Born’s criterion for melting,\(^26\) and the recently-developed bond–order–length–strength (BOLS) correlation mechanism\(^27\) for the size dependence of nanostructures has allowed us to derive an analytical solution, which has enabled us to reproduce the IHPR profiles of some specimens and to clarify the factors dictating the strongest size and the physical origin of the observed IHPR.
2. Principle

2.1. BOLS correlation and Born’s criterion

According to Born,\textsuperscript{26} the shear modulus of a specimen attenuates when the operating temperature is raised and the shear modulus approaches to zero at the melting point \( (T_m) \). The shear modulus \( \mu \) is related to the bulk modulus \( B \) and the Poisson ratio \( \nu \) by \( \mu = B/(2[1 + \nu]) \). Therefore, \( T_m \) is a key character to the mechanical strength of a material, in particular, for the plastic deformation detection. It is known that Young’s modulus \( (Y \sim B/3) \) of a liquid phase is nonzero, because the sound velocity \( v \propto (Y/\rho) \). However, the liquid phase is extremely soft and highly compressible when it is being pressed or stretched. Hence, Born’s criterion is more applicable to the compressibility in plastic deformation rather than elastic deformation. Hence, the separation between \( T_m \) and the temperature of operation \( T \), or their ratio, \( T/T_m \), is critical to the mechanical behavior of a material. If one could raise the operating temperature or lower the \( T_m \) artificially by reducing the solid size,\textsuperscript{27} the materials will become softer.

The BOLS correlation mechanism indicates that\textsuperscript{27}:

(i) If one bond breaks, the remaining neighboring ones become shorter and stiffer. The broken bond causes local strain (contraction) and quantum trapping (potential well depression) nearby the broken bond (see Fig. 1(b)). Hence, densification of charge, energy, and mass takes place in the surface skin, which serves as a pinning center, inhibiting the motion of atomic dislocations.

(ii) On the other hand, the broken bonds will lower the atomic cohesive energy of the under-coordinated atoms (the product of bond number and the bond energy), which dictates the critical temperatures for phase transition such as melting and evaporation. The cohesive energy also determines the activation energy for atomic dislocation or diffusion. Therefore, defects also provide sites initiating structure failure.

Figure 1(a) illustrates the core-shell structure of a nanograin of \( K \) radius with strained surface skin of 2–3 atomic diameter thick and Fig. 1(b) shows the correspondingly depressed quantum potential well. Recent measurement using cohesive electron beam diffraction confirmed that the bond contraction of Au nanoparticles extends only to the outermost two atomic layers.\textsuperscript{28} The under-coordinated atoms in the skin are the key to nanostructures; yet, atoms in the core interior retain their bulk nature. Because of the broken surface bonds and the broken-bond-induced local strain and quantum trapping, the energy density in the surface skin is higher, and the atomic cohesive energy of the less-coordinated surface atoms is lower compared with those in the core interior. It is known that the mechanical strength is proportional to the energy density and the melting point is proportional to the atomic cohesive energy. Therefore, the surface shell is harder at low temperatures because of the localized high energy density; yet, the skin melts more easily because of the lowered atomic cohesive energy. When the temperature approaches surface melting, the surface atoms dislocate more easily, and hence the skin is much softer than the grain interior. As the grain size is decreased, the skin effect will be increasingly dominant because of the increased proportion of the under-coordinated atoms.

2.2. Relative stress and modulus at a surface

Intrinsically, the stress, flow stress or hardness for plastic deformation, and the bulk modulus for plastic deformation are the same in dimensions and in the same unit of Pa, or J/m\(^3\), and are proportional to the sum of bond energy per unit volume.\textsuperscript{29} This intrinsic feature is nothing to do with the real process of deformation whether it is reversible or irreversible. However, in the plastic deformation, processes of activation and inhibition of the motion of atomic dislocations are involved in couple, which make the hardness or the follow stress to be different from the elastic modulus in observations. Consideration of the process of inhibition of dislocation motion is insufficient. For a complete model, one also needs to consider the activation of the dislocation and factors dominating the activation energy for the motion of dislocations.

For a given specimen, the nature and the total number of bonds remain unchanged before phase transition. However, the length and strength of the involved bonds vary with external stimulus such as the coordination environment and the operating temperature. Therefore, we need to merely consider...
where $\eta_1/\eta_B$ value of 3.37 has been obtained for an impurity-free gold monatomic chain.\textsuperscript{14} The $B_i$ and $P_i$ depend uniquely on the bond length and bond energy that vary with the coordination environment ($T_{m,i}, \alpha$), bond nature ($m$), and the relative temperature ($T/T_{m,h}$).

2.3. IHPR: The strongest size and quasimolten state

By substituting the size- and bond-nature-dependent $\eta_1(x), d(x), T_{m}(x,m)$ for the $\eta_1$, $d$, and $T_{m,i}$ in Eq. (3), we can readily obtain the size, bond nature, and temperature dependence of the mechanical strength of a nanosolid

$$P(x, \alpha) = \frac{\eta_1(x) \left( \frac{d(x)}{d(x,T)} \right)^3 \times T_{m}(x,m) - T}{T_{m}(0) - T} = P(x)/P(0) \phi(d, x, m, T).$$

The additional term $\phi(d, x, m, T)$ to the conventional HPR, $P(x)/P(0)$, covers contributions from the bond nature, the temperature $T$, the size $x$, and the melting point $T_{m}(x,m)$ of a nanocrystal, which are in the form of

$$\frac{d(x)}{d(0)} = 1 + \Delta_d(x)$$

where $\Delta_d(x) = \sum_{i \in \alpha} \gamma_i(x) \times (c_i - 1)$; $\gamma_i = \text{the bond nature indicator.}$

By comparing the currently derived form Eq. (4), with the traditionally $T$-independent HPR,
Eq. (4), one can readily find the relation
\[
\frac{n_1(x)}{n_1(0)} \cdot \frac{P(x)}{P(0)} = 1 + Ax.
\]
This term represents the classical HPR in which the activation and inhibition of atomic dislocation motion should contribute in couple.

Incorporating the activation energy for the motion of atomic dislocations, \( E_A \propto T_m \), into the prefactor \( A \), we can obtain the analytical-expression for the size, bond nature, and temperature-dependent HPR:
\[
\frac{P(x, T)}{P(0, T)} = \frac{n_1(x)}{n_1(0)} \left( \frac{d(0)}{d(x)} \right)^{-3} \frac{T_m(x, m) - T}{T_m(0) - T}
= \frac{n_1(x)}{n_1(0)} \left[ 1 + \Delta_d(x) \right]^{-3} \frac{T_m(0)[1 + \Delta_d(x, m)] - T}{T_m(0) - T}
= \frac{1}{1 + \Delta_d(x, m)} \left[ 1 + \Delta_d(x, m) \right]^{-1} \left[ 1 + \Delta_d(x, m) \right]^{-1} \left[ 1 + \Delta_d(x, m) \right]^{-1}, \quad (6a)
\]
with
\[
A(x, \theta(x)) = A_0 \exp \left[ \frac{T_m(x)}{T} \right] = A_0 \exp \left[ \frac{1 + \Delta_d(x, m)}{\theta(T)} \right], \quad (6b)
\]
where \( \theta(T) = T/T_m(0) \) is for numerical simplification. The prefactor \( A_0 \) is an adjustable parameter.

The expression indicates that:

(i) The IHPR originates from the size-induced change of the mean bond length (\( \Delta_d(x) \)) and the melting temperature \( T_m(\Delta_d(x)) \) of the specimen. At sufficiently large sizes, the \( \Delta_d(x, m) \) and the \( \Delta_d(x) \) approach to zero, and the derived form converges to the conventional HPR.

(ii) The competition between the cohesive energy loss, \( \Delta_d(x, m) \), and the energy density gain, \( n_1(x)/d_1(x) \gg 1 \) of the nanograins, and the competition between the activation (\( E_A \propto T_m(x) \) drops with \( K \)) and inhibition (\( x \) or \( K^{-1/2} \) increases) of dislocations dictate the IHPR trend.

(iii) It is further clarified that the parameter \( A \) in the HPR is replaced by \( A_0 \exp(T_m(0)/T) \), and the classical HPR becomes \( P/P_0 = 1 + A_0 \exp(T_m(0)/T) \), representing the competition between the activation and inhibition of dislocation motions.

According to this solution, GB is harder at temperatures far below \( T_m(x, m) \), because of the dominance of energy density gain, whereas at temperatures close to \( T_m(x, m) \), GB is softer than the grain interior because of the dominance of the atomic cohesive energy loss that lowers the barrier for atomic dislocation motion. Hence, the current form supports all the explanations given by the available models.

The strongest size, \( x_c(A, \theta(T), m) \), and the dominating factors for the strongest size, can be determined by the relation, \( d(\ln(P/P_0))/d(\ln x) = 0 \):
\[
d(\ln(P/P_0))/d(\ln x) = x d(\ln(P/P_0))/dx
= A(x, \theta(x), m)
\times \frac{\theta(0) + 2\Delta_d(x, m)}{\theta(0)[1 + A(x, \theta(x), m)]}
- \frac{6\Delta_d(x)}{1 + \Delta_d(x) + 2\Delta_d(x, m) - \theta(0)}/0,
\]
where \( P \) represents \( P(x, \theta(x)) \), and \( P_0 \) represents \( P(0, \theta(0)) \).

As discussed above, a nanoparticle becomes softer with respect to the bulk if the grain is sufficiently small. It is necessary to define the critical temperature, \( T_C \), for the solid–quasimolten and quasimolten–liquid transition as follows:
\[
\frac{P(x, T_C)}{P(0, T_C)} = \frac{1 + A(x, \theta(T_C), m)}{[1 + \Delta_d(x)]^3}
\times \frac{1 + \Delta_d(x, m)}{1 - \theta(0)} = 0,
\]
where \( \{ \text{Quasimolten} \} \), \( 1 \) (Quasimolten), and \( 0 \) (Liquid).

At temperatures higher than \( T_C \), the solid is softer and easily compressible compared with the bulk counterpart at the same temperature. At \( T_m(x, m) \) or higher, the nanograin becomes liquid that is extremely soft and highly compressible, complying with Born’s criterion for melting. As it will be shown shortly, \( T_C \) for solid–quasimolten transition is size-dependent and it is much lower than \( T_m \).
3. Results and Discussion

3.1. Characteristics of nanograin

Figure 2 shows the BOLS reproduction of the size-induced energy density gain represented by the modulus enhancement of ZnO nanowires, and the cohesive energy loss represented by the melting point depression of Al and Sn plates and the evaporating temperature depression of Au and Ag dots. Prediction also agrees with the size trend of Young’s modulus enhancement for Ag nanowires and the measured inward surface relaxation and the mean lattice contraction of nanostructures. These observations evidence the impact of the under-coordinated atoms in the surface skins of nanostructures to the size-induced property change. The broken bonds seemed to contribute not directly to observations, but the consequence of bond breaking is indeed profound and significant. Interested readers can refer to Ref. 27 for more details regarding the size effect on the thermal and chemical stability, lattice dynamics, optical emission and absorption, electronic, dielectric and magnetic behavior of nanostructures that consistently follow the BOLS predictions.

3.2. Phase diagram: Quasimolten state

Equation (8) gives rise to the $T_C$–$K$ phase diagram that contains the outstanding regions of solid, quasimolten, and liquid states, as shown in Fig. 3(a). The two $T_m$–$K$ profiles being overlapped are derived from the BOLS correlation (Eq. (5)) and the Born’s criterion for melting (Eq. (8)). For a given size, $T_C$ is much lower than $T_m$. $T_C$ drops even faster than $T_m$ when the solid size is reduced. This prediction is much the same as that defined by Marks.

For a Cu nanosolid with $K = 10$ (≈5nm in diameter), for example, the bond contracts by a mean value of 5%, associated with a 25% drop of $T_m$.
Figure 3(b) shows temperature dependence of $P/P_0$ for (a) Ni and (b) TiO$_2$. The solid lines are the current values. The dashed lines only consider the competition between the activation and the inhibition of atomic dislocations motion represented by $(1 + A_0 x \times \exp(T_m(x)/T))$ though the term $\varphi(d, T, m)$ is necessary.

Based on Eqs. (5) and (7), with the atomic diameter ($\text{mean diameter for an alloy}$) and the bulk $T_m$ as input parameters, we have also estimated the strongest sizes for some samples at room temperature. As listed in Table 1, the predicted critical sizes by $(1 + A_0 x \times \exp(T_m(x)/T))$ though the term $\varphi(d, T, m)$ is necessary.

Based on Eqs. (5) and (7), with the atomic diameter ($\text{mean diameter for an alloy}$) and the bulk $T_m$ as input parameters, we have also estimated the strongest sizes for some samples at room temperature. As listed in Table 1, the predicted critical sizes

$$T_m$$ and a 50% drop of $T_C$ with respect to the bulk $T_{m(0)}$ (1358 K). The 5-nm-sized Cu being in a quasimolten state at 680 K or above will be softer than the bulk counterpart at the same temperature. This understanding may explain why the strength of 300-nm-sized Cu nanograins drops by 15%, associated with a substantial increase of the ductility measured at 500 K. On the other hand, the self-heating in operation should raise the actual temperature and hence cause further softening of the specimen. In the contacting mode of plastic deformation testing, the bond breaking and deforming will release energy that will heat up the specimen considerably. Hence, the size-induced $T_C$ drop and the self-heating in operation provide mechanisms for the softening in the IHPR and the high ductility measured at $T>\theta_D$.

Figure 3(b) shows temperature dependence of the relative hardness of metallic particles of two critical sizes. The hardness drops quickly when the temperature is raised. At the quasimolten state, $P/P_0$ is smaller than unity. At $T_m$, $P/P_0$ approaches zero. Compared to the nonlinear $P/P_0 - T$ relationship, $Y/Y_0$ depends linearly on $T/\theta_D$ at $T>\theta_D$ because of the absence of the competitive processes of activation and inhibition of atomic dislocations in the hardness measurement.

### 3.3. IHPR and the strongest size

Calculations using Eqs. (5) and (6) were performed on Ni, NiP, TiO$_2$, and NiP nanograins with the standard bulk $d$ and $T_m$ values and $T = 300$ K as input. The prefactor $A_0$ is adjusted under the constraint that the slope of the traditional HPR (straight lines) should match the observations and the curve should intercept at the positive side of the vertical axis. For comparison purposes, the theoretical curves were normalized with the calculated peak values at $x_{C1}$, and the experimental data measured at room temperature were normalized with the measured peak values.

Figure 4 shows the reproduced IHPR for the given specimens. The solid lines are the current IHPR using the same $A_0$ value for the corresponding HPR. The dashed lines only consider the competition between the activation and inhibition of dislocations with the term $\varphi(d, m, x, T) = 1$ in Eq. (4), being quite the same to the approach of Zhao et al. Reproduction of the measured data evidences the validity of IHPR that is dominated by the competition between the activation and the inhibition of atomic dislocations motion represented by $(1 + A_0 x \times \exp(T_m(x)/T))$ though the term $\varphi(d, T, m)$ is necessary.

Based on Eqs. (5) and (7), with the atomic diameter ($\text{mean diameter for an alloy}$) and the bulk $T_m$ as input parameters, we have also estimated the strongest sizes for some samples at room temperature. As listed in Table 1, the predicted critical sizes

<table>
<thead>
<tr>
<th>Element</th>
<th>Measured $D_C$ (nm)</th>
<th>Predicted $D_C$ (nm) $(A_0 = 0.5, m = 1)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe</td>
<td>18.2</td>
<td>19.1</td>
</tr>
<tr>
<td>Ni</td>
<td>17.5</td>
<td>18.8</td>
</tr>
<tr>
<td>Cu</td>
<td>14.9</td>
<td>16.1</td>
</tr>
<tr>
<td>Zn</td>
<td>17.2</td>
<td>18.5</td>
</tr>
<tr>
<td>Pd</td>
<td>19.9</td>
<td>20.8</td>
</tr>
<tr>
<td>Si</td>
<td>9.1</td>
<td>10.6 $(m = 4.88, A_0 = 0.1)$</td>
</tr>
<tr>
<td>NiP</td>
<td>7.9</td>
<td>8.9 $(m = 4)$</td>
</tr>
<tr>
<td>NiZrO$_2$</td>
<td>17.0</td>
<td>19.8 $(m = 4)$</td>
</tr>
<tr>
<td>TiO$_2$</td>
<td>22.5</td>
<td>23.1 $(m = 4, A_0 = 0.01)$</td>
</tr>
</tbody>
</table>
are within 8–35 nm, agreeing exceedingly well with the documented results in the literature.

3.4. Strongest size: Dominating factors

Figure 5 plots the strongest size $K(x_c^{-2})$ dependence on the factors of $A_0$, $m$, and $T/T_m(0)$. The plots reveal the following:

(i) The measured strongest size is not a constant but varies sensitively to the parameters of $m$ and $T/T_m(0)$.

(ii) The $x_c$ depends less on the $A_0$ value if the $T/T_m(0)$ ratio is smaller than 0.2, which means that the critical size measured at very low temperature is intrinsic and varies only with the bond nature. At relatively higher temperatures, extrinsic factors become non-negligible.

(iii) When the operation temperature is raised from 0 to $T_m(x)$, the strongest size drops from maximum to minimum and then turns up with the temperature in a “U” shape. Therefore, it is not surprising why the reported critical sizes for the same specimen vary from source to source, because the operating temperature is different. A slight change of $T/T_m$ value may lead to substantial different sizes.

(iv) For a given critical size, there are at least two $T/T_m(0)$ values. However, the mechanical strengths of the same critical size obtained at different temperatures are completely different, as illustrated in Fig. 5(b).

The predicted $m$, $A_0$, and $T/T_m(0)$ dependence of $x_c$, $T_c(z)$, and the temperature trends of mechanical strength and compressibility/extendibility coincide exceedingly well with the cases as reported by Eskin et al.\(^\text{49}\) on the grain-size-dependence of the tensile elongation (extendibility) of an $A_0$, $0.4$Cu alloy in the quasimolten state. The ductility increases exponentially with temperature until infinity at $T_m$ that drops with solid size. On the other hand, the ductility increases generally with grain refinement. This is also the frequently observed cases such as the size-enhanced compressibility of alumina\(^\text{50}\) and PbS\(^\text{51}\) in nanometer range at room temperature.\(^\text{52,53}\) The predicted trends also agree with experimental observations\(^\text{54}\)

3.5. Correlation between elasticity and hardness: Shape dependence

There has been a long perception that the elastic deformation is completely different from plastic deformation in terms of process. The elastic process is reversible while the plastic is irreversible. Indeed, plastic deformation is dominated by activation and inhibition of dislocations, and it is more process-dependent. Intrinsically, the analytical expressions for elasticity, stress, and hardness, are identical in nature and in the same unit. The extrinsic competition between activation and inhibition to the motion of atomic (or glide) dislocations in the plastic deformation differ, in the hardness, from the elastic modulus or residual stress substantially. Such competition is absent from the elastic
Factors Controlling the Strongest Sizes in the Inverse Hall–Petch Relationship

4. Summary

An analytical solution has been developed for the plastic yield strength of nanograins by a combination of the BOLS correlation, Born’s criterion, local bond average, and the conventional HPR based on the following physical constraints: (i) mechanical enhancement happens at the site surrounding a defect or at the surface because of the broken-bond-induced local strain and quantum trapping; (ii) melting point suppression at sites near the defects because of the atomic cohesive energy loss; (iii) atomic dislocation requires activation energy that is proportional to the melting point.

Reproduction of the observed HPR and IHPR profiles has enabled us to gain deeper insight into atomistic origin of the IHPR and to identify the factors dominating the strongest sizes. Conclusions
can be drawn as follows:

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

(ii) The measurable IHPR is dominated by the competition between activation and inhibition of atomic dislocations. The energy-density gain in the surface skin and the effect of strain work hardening are responsible for the inhibition of atomic dislocations; yet, the cohesive-energy loss caused by the under-coordinated GB atoms dominates the activation energy for the dislocations.

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

(iv) The self-heating during detection and the size-induced presence of the soft quasimolten phase are responsible for softening in the IHPR and for the superplasticity of a metallic nanosolid.

(v) The IHPR critical size is predictable. The critical size is dominated intrinsically by the nature of the bond involved, the $T/T_m$ ratio, and extrinsically by experimental conditions or other factors such as size distribution and impurities that are represented by the factor $A_0$.

(vi) The IHPR at larger solid size converges to the normal HPR that holds its conventional meaning of the accumulation of atomic dislocations that resist further plastic deformation. The slope in the traditional HPR is suggested to be proportional to $\exp(T_m/T)$, which addresses the relationship between the hardness and the activation energy for atomic dislocations. The $K_j$ in the conventional HPR should represent the accumulation of atomic dislocations that resists further dislocations.

Acknowledgments

Financial support from NSF of China (Nos. 10772157 and 10525211), Ministry of Education (RG14/06), Singapore, and Wong KC Educational Foundation, Hong Kong is gratefully acknowledged.

References

1. E. Q. Hall, Proc. Soc. London B 64, 747 (1951);
Factors Controlling the Strongest Sizes in the Inverse Hall–Petch Relationship

56. Z. Ma, S. Long, Y. Pan and Y. Zhou, personal communication.