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Hardness of metallic crystals

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Abstract. **This paper presents a new formula for calculating the hardness of metallic crystals, resulted from the research on the critical grain size with stable dislocations. The formula is $H = 6\,kG/[\pi(1-\nu)e^{\eta}]$, where H is the hardness, k the coefficient, G the shear modulus, ν the Poisson's ratio, η a function of the radius of an atom (r) and the electron density at the atom interface (n). The formula will not only be used to testify the critical grain size with stable dislocations, but also play an important role in the understanding of mechanical properties of nanocrystalline metals.**

Keywords. **Hardness; metallic crystals; dislocation; electron density.**

1. Introduction

The well-known Hall–Petch relationship predicts that the strength or hardness of conventional metal alloys increases with decreasing grain sizes. However, the relationship fails when the grain size is down to nanometers as many experimental results have shown (EI-Sherik *et al* 1992; Ren *et al* 2004; Siegel and Fougere 1995; EI-Sherik *et al* 2005). In order to explain this phenomenon, the critical grain sizes with stable dislocations (the critical sizes of dislocation hereafter) in some metals were brought forward. Gryaznov *et al* (1989) raised the critical sizes of dislocation in 5 kinds of metals (Gryaznov *et al* 1989) and modified the critical sizes of dislocation (Gryaznov *et al* 1991). They found that the characteristic length of dislocation stability in Cu and Ni are 38 nm (sphere) or 24 nm (cylinder) and 16 nm (sphere) or 10 nm (cylinder), respectively. Nieh and Wadsworth (1991) provided the critical sizes of dislocation in 6 kinds of metals and compounds; the sizes of Cu and Ni are 19·3 nm and 2·5 nm, respectively. Wang *et al* (1995) defined the critical sizes of dislocation in 4 kinds of metals; the size of Cu and Ni are 1·7–39·4 nm and 1·3–25·6 nm, respectively. Cheng and Cheng (2001) declared the critical size of dislocation in 15 kinds of metals, the size of Cu and Ni are 1·84 μm and 3·18 μm, respectively. The different author's critical sizes of dislocation are listed in table 1. As shown in table 1, Cheng's results are far away from others'.

The physical measurements of the critical sizes of dislocation of these metals were provided by Misra *et al* (1998), Ke *et al* (1995) and Schuh *et al* (2002) in their articles (Misra *et al* 1998; Ke *et al* 1995; Schuh *et al* 2002). The values did not agree with these above-calculated values and the accuracy and uncertainties of the measured values are not known either. However, the measured values are in the same range of the 10–50 nm, more or less the same as most authors, but far away from Cheng's results. Since Cheng's method seems reasonable, efforts were made to check how to modify Cheng's formulas and parameters and thus the results would be similar to the measured values. This is a big challenge. The four authors (table 1) all got the critical sizes of dislocation for some metals; Cheng's deduction and Nieh's deduction were modified to derive a new formula of the hardness of metallic crystals for the above purpose.

2. Formulae

2.1 *Cheng's derivation process of the critical grain size*

Cheng and Cheng (2001) thought that an elastic stress field will exist around dislocations after they are formed. The attraction pressure P produced by the potential of the inner core balances the repulsive pressure. On removing the ion core, electrons will be induced to the external boundary of the void, thus producing an attraction

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Table 1. The critical sizes of dislocation from different authors.

Material	Calculated (nm)				Measured (nm)
	Gryaznov	Nieh	Wang	Cheng	
Al	11, 18	–	1·2–59·3	6960	–
Cu	24, 38	19·3	1·7–39·4	1840	< 50 (Misra *et al* 1998)
Ni	10, 16	2·5	1·3–25·6	3180	12–14 (Schuh *et al* 2002)
Pd	–	11·2	1·8–75·3	–	–
α-Fe	2, 3	–	–	1000	–
Au	–	–	–	250	10 (Ke *et al* 1995)

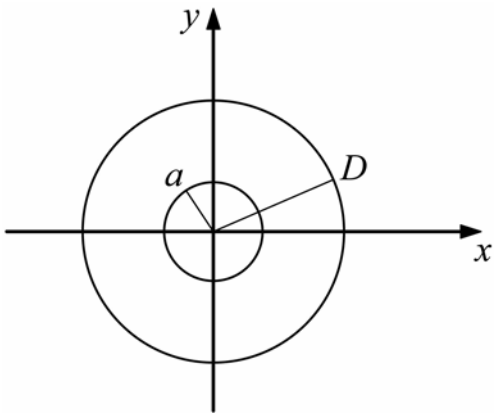

Figure 1. Schematic diagram of an edge dislocation in the x–y plane (Cheng and Cheng 2001).

counterbalancing the expanding pressure of the shell of electrons. This shows that only part of the total volume of the void is occupied by electrons. The size of an edge dislocation can be described by the outer and inner radii D and a, respectively, as shown in figure 1.

The elastic energy per unit length E_L of the dislocation between D and a is given as

$$E_L = \frac{\mu b^2}{4\pi(1-\nu)}\left[\ln\frac{D}{a} - \frac{D^2-a^2}{D^2+a^2}\right], \quad D \gg a, \tag{1}$$

where μ is the shear modulus, b the Burgers vector and v the Poisson's ratio.

According to solid physics, the pressure of electrons gas P is given by

$$3P = 2K + V_{ex}, \tag{2}$$

where K is the kinetic energy density of electrons at the boundary of atoms, and V_{ex} the exchange energy density. The pressure P can be explicitly written as

$$P = \frac{1}{3}\left\{\frac{2\times 3h^2}{10m}\left(\frac{3}{8\pi}\right)^{2/3} n^{5/3} - \frac{1}{4\pi\varepsilon_0}e^2\left(\frac{3}{\pi}\right)^{1/3}\frac{3}{4}n^{4/3}\right\}, \tag{3}$$

where n is the electron density at interfaces of atoms, m the mass of electron, h the Plank constant, ε_0 the permittivity of vacuum and e the electron charge.

Work E_P is done by this pressure in the creation of holes of dislocation per unit length with a volume V in every plane

$$E_P = -PV/d. \tag{4}$$

Here V is the volume of electrons corresponding to those driven into the void of an atom of dislocation by the environment and d is the distance between two neighbouring holes.

A close-packed structure with the length of each layer d is considered, then

$$d = 2r(2/3)^{1/2}. \tag{5}$$

The value $V \cdot n$ is equal to the valence z, i.e.

$$V \cdot n = z. \tag{6}$$

The total energy ε expanded in the creation of a unit length of dislocations is the sum of the values from (1) and (4)

$$\varepsilon = E_L + E_P. \tag{7}$$

On account of the meta-stability of dislocations, ε must be positive. Equation (7) is thus capable of yielding the ratio D/a, giving the limit in the sizes of the dislocations. Combining (1)–(7), one obtains the size limit as follows (Cheng and Cheng 2001)

$$D = ae^{\eta+1}, \tag{8}$$

$$\eta = \frac{100(1-\nu)}{\mu^*} zr^{*-3} n^{*2/3}\,(1 - 0{\cdot}546 n^{*-1/3}), \tag{9}$$

where

$$n^* \equiv n10^{-29}, \quad r^* \equiv n10^{10}, \quad b = 2r, \quad \mu^* \equiv \mu 10^{-10}, \quad a \cong r.$$

In (1), it is more reasonable to substitute the total energy of an edge dislocation per unit length for the elastic energy of an edge dislocation per unit length. The total energy of an edge dislocation per unit length can be expressed as (10) (Yu 2000)

$$E_L = \frac{\mu b^2}{4\pi(1-\nu)}\ln\frac{2D}{a}. \tag{10}$$

Thus we obtain (11) and (12) by combining (2)–(7) and (10)

$$D = \frac{1}{2} a e^{\eta}, \tag{11}$$

$$\eta = \frac{96{\cdot}9(1-\nu)}{\mu^*} z r^{*-3} n^{*2/3} (1 - 0{\cdot}523 n^{*-1/3}). \tag{12}$$

Applying (11) and (12) to copper, assuming $z = 1$, $n^* = 2{\cdot}934$ m^{-3}, $r^* = 1{\cdot}413$ m, $\mu^* = 4{\cdot}79$ Pa (Cheng and Cheng 1996), $\nu = 0{\cdot}31$, then $2D = 88$ nm. The calculated value is relatively close to the measured values. To nickel, assuming $z = 2$, $n^* = 3{\cdot}195$ m^{-3}, $r^* = 1{\cdot}382$ m, $\mu^* = 8{\cdot}00$ Pa, $\nu = 0{\cdot}34$ (Cheng and Cheng 1996), then $2D = 663$ nm. This result is rather far away from the measured values. The possible reason related to the value of n^* will be studied in more detail in our future work.

2.2 *Nieh's derivation process of the critical grain size*

There are only two edge dislocations as shown in figure 2, where l is the distance between the two dislocations, σ_{app} the externally applied stress.

The repulsive force per unit length between two edge dislocations f is given by

$$f = \frac{Gb^2}{2\pi(1-\nu)} \cdot \frac{1}{l}, \tag{13}$$

where G is the shear modulus, b the Burgers vector and ν Poisson's ratio. These two dislocations will move to their equilibrium positions when the repulsive force between them is cancelled out by the externally applied force $\tau_{app} b$, where τ_{app} is the applied shear stress, i.e.

$$f = \tau_{app} b. \tag{14}$$

Assuming that the hardness, H, is about $3\sigma_{app}$ and $\tau_{app} \sim (\sigma_{app}/2)$, then the equilibrium distance (also called the critical grain size), l_c, between the two edge dislocations can be obtained from the following formula (Nieh and Wadsworth 1991)

$$l_c = \frac{3Gb}{\pi(1-\nu) \cdot H}. \tag{15}$$

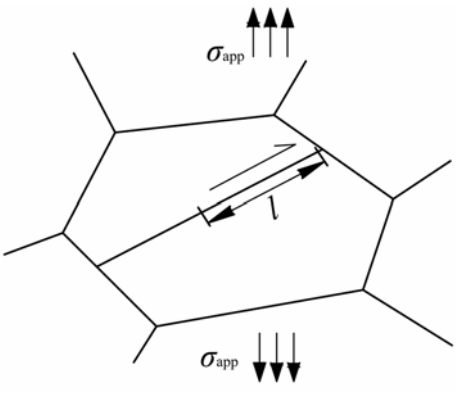

Figure 2. Dislocation pile-up at grain boundaries (Nieh and Wadsworth 1991).

3. Results and discussion

3.1 *The hardness formula of metallic crystals*

Equation (15) defined the critical sizes of dislocation, l_c, which is the same as $2D$, expressed in (11). The properties, one from the force perspective, the other from energy, should be the same. Thus, a coefficient k can be introduced. If $2D = k \cdot l_c$, then combining (11), (15) and $b = 2r$, one has

$$H = \frac{6kG}{\pi(1-\nu)e^{\eta}}, \tag{16}$$

where

$$G = \mu = \frac{E}{2(1+\nu)},$$

k is the coefficient, ν the Poisson's ratio and

$$\eta = \frac{96{\cdot}9(1-\nu)}{\mu^*} z r^{*-3} n^{*2/3} (1 - 0{\cdot}523 n^{*-1/3}).$$

3.2 *The physical significance of the components of the hardness formula*

From (16), we could know that hardness H is the function of electron density n and the radius of atom r. The relationship of r and n from Thomas–Fermi–Dirac (TFD) model is

$$n(x) = \frac{z}{4\pi\mu^3} \left[\varepsilon + \left(\frac{\psi}{x} \right)^{1/2} \right]^3, \tag{17}$$

where $\mu = a_0 (9\pi^2/128Z)^{1/3}$, a_0 is Bohr radius, Z the atomic number, $\varepsilon = (3/32\pi^2)^{1/3} Z^{-2/3}$, x the dimensionless atomic radius, $r = \mu x$ the actual atomic radius, and $n(x)$ the electron density. ψ is called the TFD function satisfying famous TFD equation, namely,

$$\frac{\mathrm{d}^2\psi}{\mathrm{d}x^2} = x \left[\varepsilon + \left(\frac{\psi}{x} \right)^{1/2} \right]^3. \tag{18}$$

The boundary condition of (18) is

$$\psi(0) = 1, \tag{19}$$

$$x_0 \frac{\mathrm{d}\psi(x_0)}{\mathrm{d}x_0} = \psi(x_0). \tag{20}$$

The relationship of n and r is shown in figure 3. For one certain atomic radius r_0, there exists one electron density distribution curve, n'–r', corresponding to (17) and (18). When the atomic radius changes from r_0 to $r_0 + \Delta r$, the relevant electron density distribution curve turns into a

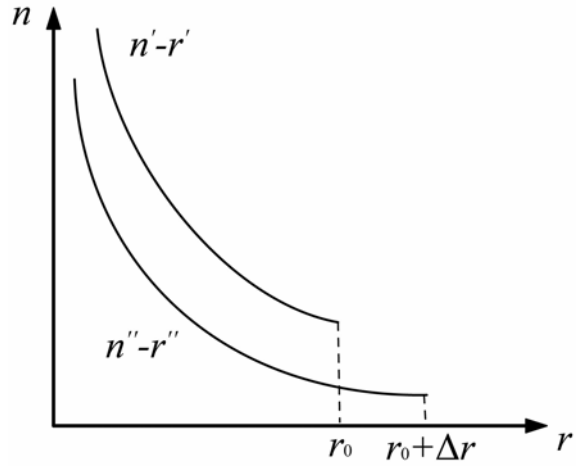

Figure 3. Effect of atomic radius variation on electron density (Li 2004).

completely new one, n''–r''. The relationship of H and n could be properly understood only after the meaning of n is understood profoundly.

3.3 *The applicable range of the hardness formula*

Deducted for metallic crystals, the formula of hardness could be applied to metallic crystals only. Since H and n are all measurable, the coefficient k could be identified. Different materials have different k values, which can be calculated with sufficient experimental data. Because the nanocrystal contains no dislocation, its expending energy is zero. H is the function of n and r. When the size of the grain is less than the critical size of the dislocation, this formula could still be applied. Thus this formula is the supplement of the Hall–Petch relationship and very useful in guiding the understanding of the mechanical behaviour of the nanomaterials.

4. Conclusions

A new formula of the hardness of metallic crystals has been given, i.e. $H = 6kG/[\pi(1 - \nu)e^{\eta}]$, on the deduction of Cheng's and Nieh's. This formula will not only be used to testify the critical grain size with stable dislocations, but also play an important role in understanding the mechanical properties of nanocrystalline metals.

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