

# On the yield stress of nanocrystals

V. G. GRYAZNOV

*Institute for High Pressure Physics of the Academy of Sciences of the CIS, Troitsk, Moscow region, 142092, Russia*

M. YU. GUTKIN

*St. Petersburg Branch of the Institute of Machine Sciences of the Academy of Sciences of the CIS, St. Petersburg, 199178, Russia*

A. E. ROMANOV

*A. F. Ioffe Physical-Technical Institute of the Academy of Sciences of the CIS, St. Petersburg, 194021, Russia*

L. I. TRUSOV

*Scientific Industrial Enterprise "ULTRAM", Krasnopresnenskaya 26, Moscow, Russia*

A generalization of the Hall–Petch relationship is proposed. The generalized relationship takes account of the contributions from intergrain sliding, generation of lattice dislocations, and influence of disclination-like defects. From this approach, a critical size corresponding to a maximum of the Hall–Petch size dependence is obtained. The value of the critical size essentially depends on the state of boundaries and it explains contradictory results for the microhardness of nanocrystals (NCs), since grain-boundary sliding is facilitated in unrelaxed nanocrystals and constrained in aged ones.

## 1. Introduction

In traditional metallic polycrystals the yield stress,  $\tau_y$ , is a structure-sensitive characteristic and at low and moderate temperatures it increases with decreasing grain size,  $d$ , according to the well-known empirical Hall–Petch law

$$\tau_y = \tau_0 + kd^{-1/2} \quad (1)$$

where  $\tau_0$  is the friction stress of the crystal lattice and  $k$  is the Hall–Petch factor. A similar law is also observed for the dependence of the yield stress on the typical size of the cell-dislocation structure in body-centered cubic (b.c.c.) metals and the alloys based on such metals. Many theoretical and experimental studies have been devoted to the physical interpretation of this dependence; the results are pretty well summarized in surveys [1–4]. For typical polycrystals with grain size ranging from 1 mm to 1  $\mu$ m the models developed are in good agreement with experimental data. However, further reduction of the scale of grain structure leads to significant deviations from the Hall–Petch law (Equation 1), which may result in a different exponent value, or a different magnitude and sign of the Hall–Petch factor. These distinctions become most apparent for the polycrystals of a new class that are sometimes called *nanocrystals* (NCs).

Investigations on the structure and properties of NCs and possible methods of their production carried out in the last ten years [5–34] testify to the fact that NCs qualitatively differ from the usual coarse-grained polycrystals. This applies, firstly, to the interfaces themselves. The interfaces in unrelaxed NCs can be up

to 1–2 nm thick. In fact, they are the interlayers of a material that often has a porosity which is higher than that of surrounding crystallites. The grains themselves, which are those domains with closely packed atoms, can be up to several nanometers in size. Lately, a comparison of the results obtained in experiments directly observing NCs by high-resolution electron microscopy (HREM) [26] with other methods – data X-ray [11] and neutron [19] diffraction, and the results of studying the structure of NCs by the EXAFS (extended-X-ray-absorption fine structure) method [22], and Mössbauer [12] and positron [13, 14] spectroscopy – allowed Wunderlich *et al.* [26] to establish that an appreciable fraction of interfaces have a highly distorted pre-boundary region with a lowered density and a somewhat elevated level of internal elastic stresses. An approximate examination of the microstructure of palladium [26] showed that it contained about 40 vol % of a non-distorted crystalline material, about 25 vol % of stretched amorphous interlayers of grain-boundary material, 25 vol % of a material with a high level of internal stresses, and about 10 vol % of pores.

The peculiarities observed in the structure of NCs, which are enumerated above, can influence the properties of NCs; in particular, they can modify the type of the dependence of the yield stress on the grain size. For example, microhardness-test experiments performed with nanocrystalline Ni [9, 23], TiO<sub>2</sub> [16, 17, 28], Cu [20, 21, 23, 32] and copper alloys [33], Pd [20, 21, 32], Co [23] and Fe [24] showed that only a several-fold increase in the yield stress,  $\tau_y$ , is observed for real materials instead of the hundred-fold increase in

the value of  $\tau_y$  that is expected from Equation 1 for materials with  $d$  as small as 10 nm. These experiments demonstrate that the value of  $\tau_0$  in Equation 1 can increase [27], and the value of  $k$  can decrease [21, 27] or even change sign [20, 29–31]. Jang and Koch, trying to find the source of the spread in the results they obtained, discovered that the microhardness of nanocrystalline iron may follow the  $d^{-1/2}$  dependence as well as the  $d^{-1}$  dependence proposed earlier by Kocks [35].

There are various attempts to use distinctive features of NCs in the literature (including their porosity, the mobility of grain boundaries, and the presence of disclinations [35–37] to account for the phenomena observed. The present paper aims to obtain a generalized empirical analogue of Equation 1 that will allow for the yield characteristics of the materials of crystallite and intercrystallite layers, without dwelling on the particular physical processes that determine the yield stress in NCs. The conditions are also determined under which the yield stress starts decreasing with decreasing grain size and becomes lower than the friction stress in crystallites.

## 2. Results

### 2.1. Yield stress of nanocrystals

Following Kocks [35], represent a nanocrystalline material as a composite of a crystalline matrix with inclusions of intercrystallite layers. The experimental value of the ratio of typical sizes of crystallites and interfaces is low enough to consider the interfaces in the matrix as thin plates which are chaotically placed and oriented. As all the possible orientations of the inclusions are equally probable, a medium with isotropic effective properties can be considered. Representing the inclusions by oblate ellipsoids, the effective shear modulus,  $G$ , of such a composite can be obtained [38]

$$G = G_m + c \frac{(G_m + \eta G_1)(G_1 - G_m)}{G_1(1 + \eta)} \quad (2)$$

where  $G_m$  is the shear modulus of the matrix,  $G_1$  is the shear modulus of the inclusion (interface)  $\eta = 0.5 [1 + 3/(4 - 5\nu_1)]$ , where  $\nu_1$  is Poisson's coefficient of the inclusion, and  $c$  is the volume fraction occupied by inclusions ( $c \ll 1$ ).

Equation 2 was obtained under the assumption that the matrix and the inclusions are elastic; no reservations were made about the ratio of their moduli. Assume that the yield stress of the matrix,  $\tau_m$ , of the inclusions,  $\tau_1$  and the effective yield stress of the composite,  $\tau_y$  are linearly connected with the corresponding shear moduli

$$G = H\tau_y, \quad G_m = H_m\tau_m, \quad G_1 = H_1\tau_1 \quad (3)$$

where  $H$ ,  $H_m$  and  $H_1$  are dimensionless factors. Additionally, assume that the values of  $\tau_m$  and  $\tau_1$  are connected with the typical structure period  $d$  corresponding to the NC grain size by the following Hall–Petch-type relationships:

$$\tau_m = \tau_m^* + k_m d^{-m/2} \quad (4a)$$

$$\tau_1 = \tau_1^* + k_1 d^{-i/2} \quad (4b)$$

where superscripts  $m$  and  $i$  are integers.

It can easily be shown (for example, for the cube-shaped grains) that the volume fraction of the inclusions may be estimated as  $c \approx 3\delta/d$ , if the thickness of interfaces,  $\delta$ , is much less than the distance,  $d$ , between the interfaces. Then substituting Equations 3 and 4 into Equation 2 the following empirical dependence of the effective yield stress of the composite on the typical structure-size,  $d$ , is obtained

$$\begin{aligned} \tau_y = & \frac{H_m}{H} \tau_m^* + \frac{H_m}{H} k_m d^{-m/2} \\ & + 3 \frac{(1 - \eta) H_m \tau_m^* + \eta H_1 \tau_1^*}{(1 + \eta) H} \delta d^{-1} \\ & + 3 \frac{1 - \eta}{1 + \eta} \frac{H_m}{H} k_m \delta d^{-(1 + m/2)} \\ & + 3 \frac{\eta}{1 + \eta} \frac{H_1}{H} k_1 \delta d^{-(1 + i/2)} \quad (5) \\ & - 3 \frac{\delta (H_m)^2}{(1 + \eta) H H_1} \frac{(\tau_m^*)^2 + 2\tau_m^* k_m d^{-m/2} + (k_m)^2 d^{-m}}{\tau_1^* d + k_1 d^{1 - i/2}} \end{aligned}$$

The next step is to choose the values of  $m$  and  $i$ . In this case one must proceed from the specific physical mechanism that determines the yield strength in each of the phases in a particular situation. Assume that  $\tau_m$  and  $\tau_1$  are governed both by the stress in the heads of the dislocation pile-ups set against the matrix–inclusion boundary from the matrix side and by the stress of the pile-ups in the “very intergrain” layer. The latter pile-ups provide a mechanism of intergrain sliding. The typical dimensions of pile-ups of both types is about  $d$ . This means that values of  $m = i = 1$  may be chosen to get the usual Hall–Petch law for both the matrix and the inclusion.

Now consider how the quantities  $\tau_m^*$ ,  $\tau_1^*$ ,  $k_m$  and  $k_1$  are related to each other. If the main distinction of the interfaces from the crystallites is the low atomic density of the former, it seems reasonable to assume that  $\tau_1^* \approx q\tau_m^*$  and  $k_1 \approx pk_m$ , where  $q$  and  $p$  are dimensionless constants smaller than 1. Evidently, the lower the atomic density of the interfaces, the smaller the values of  $q$  and  $p$ .

Finally, for the sake of simplicity take  $H \approx H_1$ . Then Equation 5 can be easily reduced to the form

$$\begin{aligned} \tau_y = & \tau_m^* + k_m d^{-1/2} \\ & - \frac{3}{1 + \eta} \frac{\delta [1 - q(1 - \eta + \eta q)] (\tau_m^*)^2 d + [2 - q(1 - \eta + \eta p) - p(1 - \eta + \eta q)] \tau_m^* k_m d^{1/2}}{q\tau_m^* d + pk_m d^{1/2}} \quad (6) \\ & + \frac{[1 - p(1 - \eta + \eta p)] (k_m)^2}{q\tau_m^* d + pk_m d^{1/2}} \end{aligned}$$

Consider in greater detail the third term on the right-hand side of Equation 6 which is accounted for by the fact that an interface is treated in our consideration as an interlayer of finite thickness with its own elastic and plastic characteristics. Taking Poisson's coefficient,  $\eta$ , to belong to the interval 0.2–0.4 gives the following estimate for the value of  $\eta$ :  $1 \leq \eta \leq 1.25$ . For simplicity, take  $\eta \approx 1$ . Hence, the atomic density of boundaries may amount for up to 70% of the ordinary density of the material [41]. At such densities the main mechanical properties of the material (the Young's modulus, the yield stress, the fatigue stress) are known to be several times worse than the characteristics of the compact body [42]. Therefore, one can estimate  $q \approx p \approx 0.2$ .

For these values of parameters  $\eta$ ,  $q$  and  $p$  the third term in Equation 6 turns out to be positive and is subtracted from the value of  $\tau_m$ . As expected, the low-density interlayers lower the yield stress of the composite. Using the above estimates for  $\eta$ , Equation 6 can be expressed in its simplest form

$$\tau_y = (\tau_m^* + k_m d^{-1/2}) \left( 1 - \frac{1 - q^2 3 \delta}{q 2 d} \right) \quad (7a)$$

or

$$\tau_y = \tau_m^* + k_m d^{-1/2} + \frac{3q^2 - 1}{2q} \tau_m^* \delta d^{-1} + \frac{3q^2 - 1}{2q} k_m \delta d^{-3/2} \quad (7b)$$

Evidently, when such a dependence is plotted in  $\tau-d^{-1/2}$  co-ordinates, the straight line in Equation 1 will remain straight only at large  $d$  or else as  $q \rightarrow 1$ . At  $q < 1$  its slope will gradually decrease with decreasing grain dimension down to some critical size,  $d_{C_1}$ , where the effective Hall–Petch factor will change sign. The critical size,  $d_{C_1}$  can easily be found from the condition  $\delta \tau_y / \delta d^{-1/2} = 0$ . This equality can be reduced to the following equation

$$(d^{-1/2})^2 + \frac{2\tau_m^*}{3k_m} d_m^{-1/2} - \frac{2}{9} \frac{q}{1 - q^2} \frac{1}{\delta} = 0 \quad (8)$$

Solving this equation

$$(d_{C_1})^{-1/2} = \frac{\tau_m^*}{3k_m} + \frac{1}{3} \left( \frac{2q}{\delta(1 - q^2)} \right)^{1/2} \times \left( \frac{(\tau_m^*)^2 \delta (1 - q^2)}{2(k_m)^2 q} + 1 \right)^{1/2} \quad (9)$$

Substituting the usual values for parameters  $\tau_m^*/k_m \approx 1 \div 100 \text{ mm}^{-1/2}$  and  $\delta \approx 1 \text{ nm}$  the following approximate expression for  $d_{C_1}^{-1/2}$  is obtained

$$(d_{C_1})^{-1/2} \approx - \frac{\tau_m^*}{3k_m} + \frac{1}{3} \left( \frac{2q}{\delta(1 - q^2)} \right)^{1/2} + \frac{(\tau_m^*)^2 (2\delta)^{1/2}}{12(k_m)^2} \left( \frac{1 - q^2}{q} \right)^{1/2} \quad (10)$$

Thus, the following estimate for the critical grain size,  $d_{C_1}$ , is obtained

$$d_{C_1} \approx \frac{9\delta(1 - q^2)/2q}{1 - 2 \left( \frac{\delta(1 - q^2)}{2q} \right)^{1/2} (\tau_m^*/k_m)} \quad (11)$$

Fig. 1 presents the family of curves,  $d_{C_1}(q)$ , calculated according to Equation 11 at  $\delta = 1 \text{ nm}$  for Ti [2], Cu [20], Fe [4], Ni [3] and Ag [43]. The corresponding values of the ratio  $\tau_m^*/k_m$  are 55, 26, 8, 4 and  $4 \text{ mm}^{-1/2}$ , respectively. The dashed line is calculated according to the approximate formula  $d_{C_1} \approx 9\delta(1 - q^2)/2q$ , which may be used for estimating  $d_{C_1}$  in practically any material. At  $q = 0.2$ , this expression yields the grain size  $d_{C_1} \approx 22\delta = 22 \text{ nm}$ , which corresponds to the volume fraction of boundaries  $c \approx 0.12$ .

Equation 7 can be used to determine the critical grain size,  $d_{C_2}$ , at which the yield stress of a composite becomes equal to the friction stress in the matrix, i.e.  $\tau_y - \tau_m^* = 0$ . This critical size turns to be equal to

$$d_{C_2} \approx \frac{3}{2} \frac{1 - q^2}{q} \delta \approx d_{C_1}/3$$

At  $\delta = 1 \text{ nm}$  and  $q = 0.2$  then  $d_{C_2} \approx 7 \text{ nm}$ .

Equation 7 turns out to agree pretty well with the different and apparently contradictory experimental data. For example, compare the results of our calculations with the data from Chokshi *et al.* [20] and Jang and Koch [27]. Rewriting Equation 7 in terms of the microhardness and substituting the values of  $H_m^*$  and  $k_m$  corresponding to coarse-grained Cu [20] and Fe [4] the families of curves,  $H(d^{-1/2})$ , are obtained (see Fig. 2a, b) for different values of  $q$ . The results given in [20] are seen to be in good agreement with the descending portion of the curve  $H(d^{-1/2})$ , the

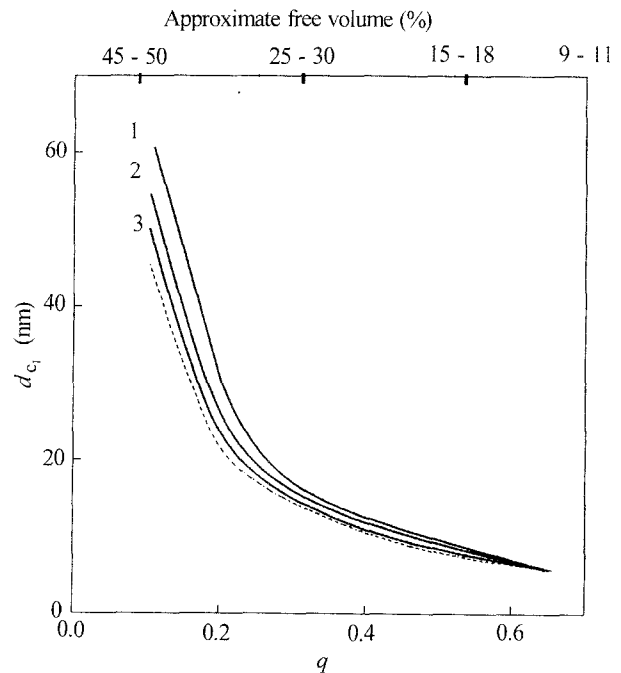


Figure 1 The dependence of the critical size of a NC grain,  $d_{C_1}$ , on the parameter  $q$  for: (1) Ti; (2) Cu; (3) Fe, Ni, Ag, (---) is an approximate curve that may be applied to any material. Parameter  $q$  was put in correspondence with the atomic density of boundaries using the data from [42].

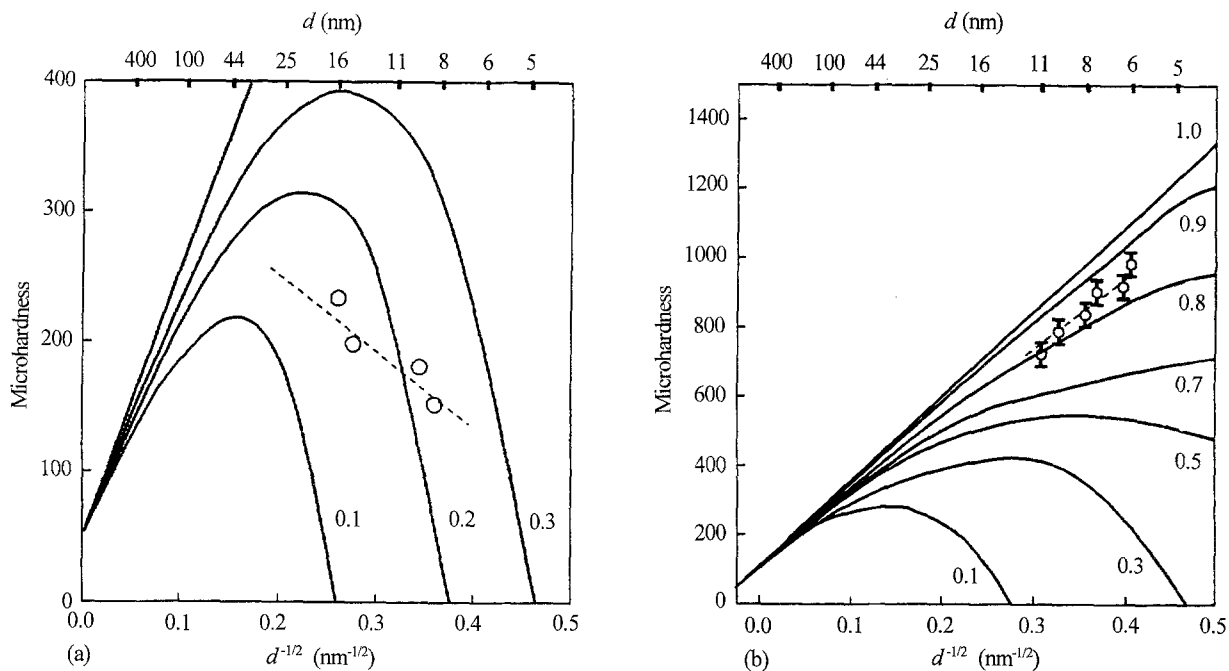


Figure 2 The dependence of the microhardness on the grain size at different atomic densities of boundaries of nanocrystalline: (a) Cu, and (b) Fe. This quantity is characterized by parameter  $q$ . The figures on the curves denote the values of this parameter. (---) straight lines drawn through the experimental points (○) [20] and (◻) [27].

difference from the calculated values amounting up to 25–45% at  $q \approx 0.2$  (see Fig. 2a). A qualitatively different increasing curve  $H(d^{-1/2})$  [27] fits well between the calculated curves for  $q = 0.8$  and  $q = 0.9$  (Fig. 2b). The difference in dependences of  $H$  on  $d^{-1/2}$  obtained in [20] and [27] seems to be caused by the fact that the measurements were carried out with samples in different stages of relaxation. The measurements in [20] were performed for a nanopowder-based, as-compacted, copper sample. The boundaries of the nanocrystallite grains in the sample thus produced correspond to the surface of the as-synthesized copper particles in the pre-compaction sample. Evidently, such a procedure of producing a nanocrystalline material predetermines the low atomic density of boundaries (which increases as the internal stresses in the sample relax). The authors of [27] measured the microhardness of separate polycrystalline particles (with sizes  $\leq 1 \mu\text{m}$ ) consisting of nanocrystallites. In this case interfaces are formed from the walls of dislocation cells generated during the ball-milling process. It is clear that such a procedure produces nanocrystalline iron in which the atomic density of boundaries is significantly higher than in the former case (according to Fig. 2b it should differ from the normal value by about 5–7%).

Therefore, we have shown that dependences of  $\tau_y$  and  $H$  on  $d^{-1/2}$ , for sufficiently small grains, can differ from the Hall–Petch relationship, Equation 1, but still be consistent with experimental data. The contradictions arising on comparison of experimental results obtained by different authors can be resolved in the framework of the approach proposed. The type of deviation from the Hall–Petch law is determined by the atomic density of the interfaces and the range of nanocrystallite sizes under study ( $d \leq d_{c1}$ ).

## 2.2. Generalized Hall–Petch relationship

The approach used above led to the dependence of the yield stress on three terms, in Equation 7b, differing in the values of the exponents ( $d^{-1/2}$ ,  $\sim d^{-1}$ ,  $\sim d^{-3/2}$ ) and in the values of constant factors in these terms. The most general relation between the yield stress and the grain size can, probably, be written in the following form:

$$\tau_y = \tau_0 + k^{(0)} \log d + \sum_{n=1}^{\infty} k^{(n)} \bar{d}^{-n/2} \quad (12)$$

This expression is a generalization of the Hall–Petch law which contains the terms accounted for by the different physical processes influencing the yield stress. The logarithmic term corresponds to the contribution to the yield stress of unrelaxed NCs by disclinations [37].

In each particular instance, depending on the material composition, the range of grain sizes, the structure and properties of boundaries, the dislocation structure, the temperature of testing, the hydrostatic stress, etc, one or several terms can come to the foreground. In this case the influence of the other terms (which can be eliminated from the expression by setting the corresponding coefficients,  $k^{(n)}$ , to zero) is negligible. For example, for typical coarse-grained polycrystals it is possible to take  $k^{(1)} = k$ , and  $k^{(0)}$ ,  $k^{(2)}$ ,  $k^{(3)}$ ,  $\dots = 0$ , while in the Equation 7b, proposed above to describe the properties of NCs,  $k^{(1)} = k_m$ ,  $k^{(2)} = (-3/2)(1 - q^2/q) \tau_m^* \delta$ ,  $k^{(3)} = (-3/2)(1 - q^2/q) k_m \delta$ , and  $k^{(0)}$ ,  $k^{(4)}$ ,  $k^{(5)}$ ,  $\dots = 0$ .

## 3. Discussion

In setting out the results of this study mention was deliberately avoided, whenever possible, of possible

mechanisms that lower the yield stress of NCs in comparison to the value expected from Equation 1. This was done because the particular causes of the high deformability of interfaces that brings about the decrease in hardness of NCs played no important role in deriving the main results, Equations 5 and 6. However, these causes become essential in the evaluation of the parameters  $m$ ,  $i$ ,  $q$  and  $p$  as well as for clarifying the physical meaning of the terms in the generalized expression, Equation 12. Below are some remarks on this.

The first concerns the experimental procedure of the microhardness test. As a rule, such measurements lead to an abrupt increase of local stresses near the indenter, which can initiate intercrystallite slipping or boundary migration leading to the local coarsening of the structure (exaggerated recrystallization) [44]. Such a situation is schematically presented in Fig. 3a and b.

In the former case an important factor is the porosity which can amount in NCs to 10–15 vol. percent when averaged over all of the volume. At such values of porosity in boundary regions, intergrain slipping should become the most efficient channel of stress relaxation [31] (Fig. 3a). This seems all the more probable as the typical time of grain slipping, for sufficiently small grains, can be shorter than the time required for the generation of dislocations inside the grain or for relaxation via the diffusion–creep mechanism. Besides, grain slipping can be present in NCs with small porosity [31], provided the boundaries are not relaxed too much. It should also be mentioned that slipping can be retarded by the residual stresses that persist in the volume of a NC after compaction. The hydrostatic local stresses under an indenter can also lock this channel of the relaxation of tangential stresses. Boundary dislocations can also provide the mechanism of such slipping. Theoretical calculations [45, 46] show that the individual lattice glissile dislocations are not stable in a polycrystal with grain size less than some characteristic value  $d^*$ , agreeing with experiments [33]. Only dislocation dipoles were observed [26] in not-fully-relaxed NC grains [26]. Relaxation of internal stresses in NCs may lead to the formation of pile-ups of boundary dislocations which raise the yield stress of the NCs. It was for this reason that the value of the exponent  $i$  was chosen to be  $i = 1$ . However, the contribution of boundary dislocations to the value of  $k$  will be smaller than ordinary lattice dislocations due to the smaller magnitude of the Burgers vector of boundary dislocations. The porosity-assisted slipping seems to be capable of providing the values of parameters  $q$  and  $p$  (which determine the ratio of  $\tau_m^*$  and  $k_m$ , and the ratio of  $\tau_i^*$  and  $k_i$ ) that lead to the negative contribution of the boundaries to the yield stress (7).

However, cases have been reported (see, for example, [47]) when the residual porosity is too small ( $< 10\%$ ) to facilitate the slipping processes in an appreciable volume near the indenter. Then, exaggerated recrystallization [48] may be observed in the regions where the hydrostatic component of local stresses is too small to suppress the creep of dislocations in the boundaries, i.e. to suppress the boundary

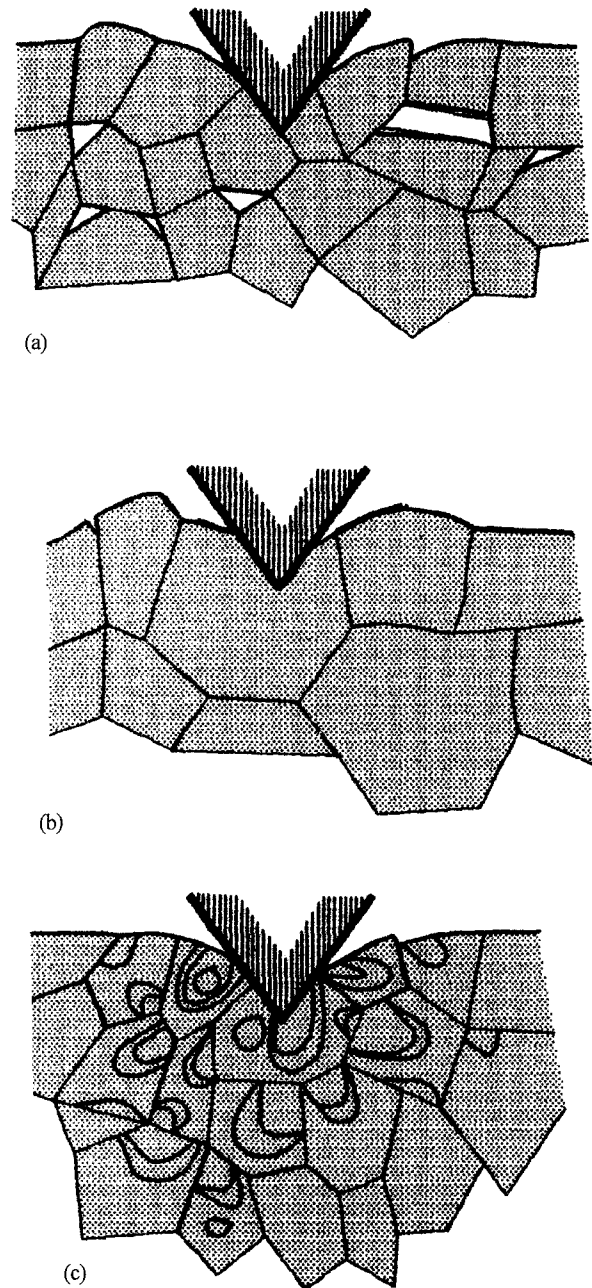


Figure 3 Models of deformation phenomena under an indenter tip in NCs: (a) densification phenomena resulting from intercrystallite sliding. Solid lines denote voids, (b) stress-induced boundary migration in the region of very intense local stresses under the indenter, and (c) generation of dislocations by interface sources when boundary migration and sliding phenomena are suppressed.

migration (see Fig. 3b). Such regions have higher concentrations of non-equilibrium vacancies [49], which can decrease the values of parameters  $q$  and  $p$ . In its turn, the fact of the creep of boundary dislocations makes the assumption  $i = 1$  reasonable. In this case the values of  $q$  and  $p$  tend to 1 in high-purity dense NCs.

If grain-boundary slipping is blocked by impurity atoms, generation of lattice dislocations becomes the main relaxation process. In this case as  $q, p \rightarrow 1$  and  $i = m = 2$  the well-known dependence first proposed by Kocks in [35] for other models is obtained; and the indenter cannot produce any noticeable imprint, since the dislocations generated return to their sources. This is very similar to observations in experiments on

nanoindentation: the smaller the indentation depth, the harder the material [50]. Besides, in this case the material was shown to demonstrate the highest hardness when the indent trace is not accompanied by the formation of dislocation rosette patterns.

The presence of the logarithmic term in Equation 12 can be associated with the pentagonal symmetry axes [51] or with the grain-boundary disclinations [36, 37]. A similar dependence may be produced by the misfit dislocations uniformly distributed over the boundary. The terms with higher powers of  $d$  ( $\sim d^{-n/2}$ ,  $n > 2$ ) may arise when averaging the contributions from grains and boundaries, as was the case with Equation 7 for  $i = m = 1$ . In addition, they may be accounted for by the singularities of the internal stress field whose scale is commensurable with the grain size.

Since the porosity of NCs depends on the temperature conditions, the coefficients in the generalized Hall–Petch relationship should also depend on the temperature; furthermore, in the presence of the phenomena of interface reconstruction and boundary migration these coefficients are noticeably time-dependent. The character of the temperature dependence of the NC yield stress is mainly determined by the nature of defects and the particular deformation mechanism.

In [16] as-compacted rutile NCs were shown to possess a Vickers microhardness higher than that of the coarser-grained samples for the whole temperature range. The fact that the observed microhardness increases with temperature is probably caused by densification processes in porous compacts.

Dense NCs behave differently. In [24] the variation of the microhardness of Pd NCs with temperature was investigated. The microhardness of nanocrystalline samples tended to decrease at small annealing temperatures,  $\sim 0.26T_m$  in contradiction to the coarse-grained samples. The averaged hardness of nanocrystalline palladium decreased slowly up to temperatures of approximately  $0.55T_m$  and then abruptly fell off (volume diffusion mass-transfer is responsible for the processes of high-temperature exaggerated recrystallization).

Such a two-stage degradation of the microhardness of NCs is accounted for by the presence of different processes near the boundaries. The first stage can be caused by the ageing of boundaries [46], and the exit of dislocations generated during compaction into interfaces. The second stage corresponds to boundary migration that, however, is of a typical character (without the contribution of non-equilibrium processes).

In conclusion, it must be stressed that in calculating the effective yield stress it does not suffice to reveal the most important physical processes influencing the yield stress inside a grain and its boundaries. Of equal importance is the need to properly superimpose these mechanisms in calculations.

#### 4. Conclusion

An expression describing the dependence of the yield stress on the grain size was proposed. The dependence

obtained is in good agreement with the data given in the literature (see the references given in the text). It was shown that for unrelaxed boundaries with low atomic density there is a critical grain size corresponding to a maximum of the curve,  $\tau_y(d^{-1/2})$ , which is confirmed by observations of negative values of the Hall–Petch factor. This critical grain size strongly depends on the quality of the boundaries and it increases with increasing boundary atomic density and is only weakly dependent on the material of the nanocrystallites. At low atomic densities in boundaries, the curve  $\tau_y(d^{-1/2})$  increases and is close to linear. However, it has a higher effective value of  $\tau_0$  and a smaller coefficient  $k$  compared to the Hall–Petch law for coarse-grained polycrystals. Therefore, the deviations from the Hall–Petch law for the new curves proposed are determined by the quality of the interfaces and the range of nanocrystallite sizes under study; i.e. the state of the boundaries, and the density and grain size are important characteristics of NCs.

A generalized Hall–Petch relationship was proposed, Equation 12, containing terms corresponding to the different physical processes that determine the yield stress of polycrystals. Consideration was given to the terms corresponding to intergrain slipping, generation of lattice dislocations and the action of disclination-like defects.

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