

Transition from microstructures to nanostructures and ultimate hardening

S.A.Firstov, T.G.Rogul, O.A.Shut

I.Frantsevich Institute for Problems of Materials Science, National
Academy of Sciences of Ukraine, Kyiv, Ukraine

Received November 17, 2009

Regularities of change in the dependence of the yield stress on grain size in transition from the microstructured to the nanostructured state are discussed. It is shown that, using S-functions, a generalized equation for the yield strength dependence on the grain size with regard to changes in the hardening mechanisms of polycrystals in the vicinity of critical grain sizes d_{cr1} and d_{cr2} can be obtained. This equation enables to describe the softening effects in transition to nanostructures (the so-called "negative" trend of the Hall-Petch relationship) and an abrupt hardening under conditions of increased intergranular cohesive strength.

Обсуждаются закономерности изменения зависимости напряжения течения при переходе от микро- к наноструктурированному состоянию. Показано, что с помощью S-функций можно получить обобщенное уравнение зависимости предела текучести от размера зерна с учетом изменения механизмов упрочнения поликристаллов в окрестности критических размеров зерен $d_{кр1}$ и $d_{кр2}$. Это уравнение позволяет описать как эффекты разупрочнения при переходе к наноструктурам (так называемый "отрицательный" ход зависимости Холла-Петча), так и, напротив, резкое упрочнение при условии повышенной прочности межзеренного сцепления.

Undoubtedly, Professor Lev Palatnik can be called among the founders of nanotechnologies and the investigation of the mechanical properties of nanostructured materials (though the word "nanomaterial" was not used at that time) because he studied in great detail the mechanical properties of thin films where either nanolayered structures or extremely small grain sizes up to amorphous structures can be obtained rather easily. In a generalizing work [1], he discussed different effects of changes in the mechanical properties of thin film objects. L.Palatnik formulated the idea that "the classification of films into "thin" and "massive" ones is conventional and acquires a clear physical meaning only when a specific structural state and a specific physical property are considered. A critical thickness h_k (or an interval of h_k) below which the parameter h influences directly the struc-

ture of the condensate can serve as a criterion of the thin film state". This idea corresponds to the modern concepts of the specificity of properties of nanostructured materials in connection with the manifestation of the specific "size" effect.

The investigation in the influence regularities of the structural element size, in particular, the grain size, on the strength of materials was always in the focus of attention. It is well established that, in a rather wide range of a polycrystalline material grain size, the Hall-Petch equation is satisfied [2–7] where the dependence of the yield strength σ_y on the grain size d can be expressed by the formula

$$\sigma_y = \sigma_0 + k_y d^{-1/2}, \quad (1)$$

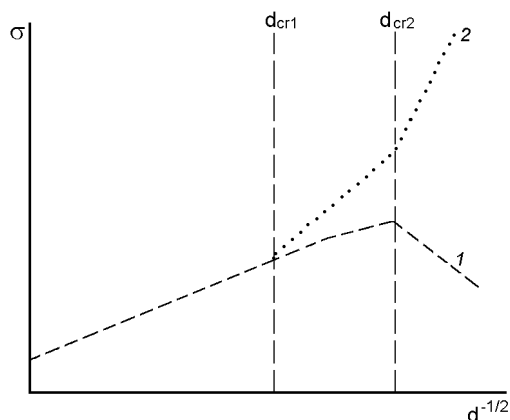


Fig. 1. Schematic dependence of the yield strength on the grain size in transition from the grain microsizes to grain nanosizes. Curve 1 corresponds to the transition from the Hall-Petch equation to a decreased strength in the nanosize range ("negative" slope) [12–18, etc.]; curve 2, to the transition to the dependence with an exponent of d of -1 at $d_{cr2} \leq d \leq d_{cr1}$, and to abrupt hardening for the grain size decreasing below d_{cr2} in the case of strong boundaries [23–25].

where the parameter σ_0 characterizes the averaged resistance to dislocation motion over the grain body and the coefficient k_y characterizes the difficulty of slip transfer through the grain boundary. A large body of experimental data confirms that in many cases, both parameters (σ_0 and k_y) are practically constant in the grain size range from several hundreds of micrometers to several micrometers. If deviations from this dependence are observed, those can be caused by either a change in the state of grain boundaries, which can be characterized by the coefficient k_y , or by a change in the resistance to dislocation motion over the grain body σ_0 due to redistribution of impurities or alloying elements between grains and grain boundaries when the grain size is varied.

Moreover, in some works [8–10] deformation-induced structures, the exponent of d in Eq.(1) was reported to vary from $-1/2$ to -1 .

In recent years, the interest to the dependences of the strength (yield strength) on the grain size is increased due to studies of the mechanical properties of nanostructured materials. The most often discussed effect lies in the fact that, instead of the successive hardening, an inverse relationship, i.e., a "negative" slope ($k_y < 0$) of the

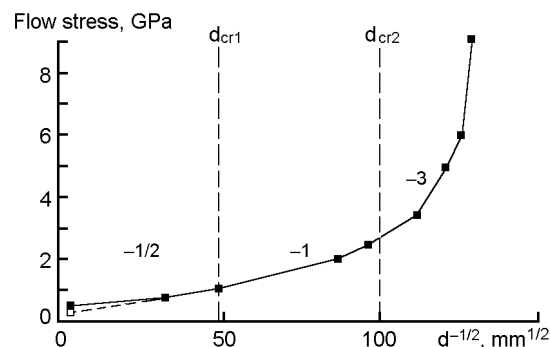


Fig. 2. The yield strength σ as a function of the grain size d in chromium obtained by magnetron sputtering [23, 24].

Hall-Petch relation is observed in the nanometer grain size range. This inverse Hall-Petch effect was observed experimentally for a number of materials [11–17, etc.], and a set of models was proposed to explain it [18–22, etc.].

In our investigations [23, 24] on materials obtained by the vacuum deposition methods, two effects were observed, namely, in transition from the microstructured to the nanostructured state, at least two critical grain sizes (d_{cr1} and d_{cr2}) were revealed in the vicinity of which the hardening mechanism changes. In particular, in the submicron grain size range $d_{cr1} \leq 1 \mu\text{m}$, the exponent of d in Eq.(1) changes from $-1/2$ to -1 occurs (Fig. 1, curve 2).

It follows from Figs. 1 and 2 that in the nanosize range ($d \leq d_{cr2}$), a drastic hardening is observed instead of a common transition to the negative slope, due to the segregation of useful impurities at the grain boundaries in thin chromium films [23, 24]. This allowed to propose a concept of "useful" impurities increasing the strength level of nanostructured materials [24, 26].

This work is aimed at the analysis of the above-mentioned effects and at an attempt to obtain a generalized dependence of the yield strength on the grain size.

1. *Transition from $-1/2$ exponent to -1 one in dependence (1) in the case of grain refinement.* For deformation-induced microstructures, such a transition was noted a rather long time ago [8–10]. In particular, after severe plastic deformations, the formation of deformation-induced ultrafine-grain structures is usually noted [27], the disorientation of individual elements in such a structure being quite comparable with characteristic disorientations of grains in a conventional polycrystalline aggregate.

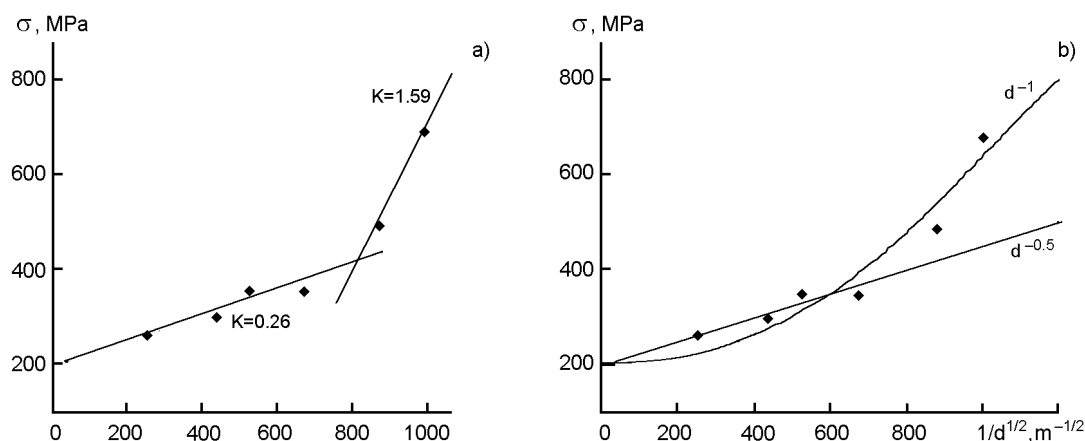


Fig. 3. Experimental dependence of the yield strength (σ) for fine-grained VT1-00 commercially pure titanium on the grain size (d) in the $\sigma(d^{-1/2})$ coordinates [32] (a); our approximation of experimental data presented in Fig. 3a using $\sigma(d^{-1/2})$ and $\sigma(d^{-1})$ dependences (b).

In [27], the concept of the critical grain-boundary angle ($\theta_{cr} > 3-5^\circ$) was introduced. When it is exceeded, the boundary of the deformation substructure exerts resistance to slip transfer which is practically equal to that exerted by the large-angle grain boundary. Later, using the improvements in the instruments and methods for the determination of such disorientations, it was shown that those can attain tens of degrees [10, 28, 29].

As noted above, for such structures, when the grain sizes of deformation origin are smaller than several micrometers, the exponent of the grain size in dependence (1) is equal to -1 , rather than to $-1/2$. Thus, at $d \leq d_{cr1}$, the following relation is actually satisfied:

$$\sigma_y = \sigma_0 + k_1 d^{-1}, \quad (2)$$

where the term σ_0 has the same meaning as in Eq.(1) and the coefficient k_1 , though characterizing also the difficulty of slip transfer through the grain boundary, has obviously other dimensionality and, therefore, a somewhat different physical meaning as compared to those of the coefficient k_y in Eq.(1).

Considering this effect, Thompson [8] postulated actually that, at grain sizes smaller than a certain critical value, the hardening described by Eq.(2) becomes more efficient. This critical grain size can be determined at the intersection point of dependences (1) and (2). Namely,

$$d_{cr1} = (k_1/k_y)^2. \quad (3)$$

In works of the authors [23–25], it was shown that the type (2) dependence is valid not only for grains of the deformation origin, but also for ultrafine-grained structures obtained using vacuum deposition technologies. In [30], it was also reported that, e.g., for a Cu–Cr multilayer composition, at a certain critical layer sizes, a knee is observed in the dependence of the yield strength on the grain size in the coordinates of Eq.(1), while in processing of the same data in the $\sigma(d^{-1})$ coordinates, dependence (2) is satisfied well. In [31], it is stated that, in the submicron grain size range (for strained iron and titanium), the dependence $\sigma(d)$ is described much better by Eq.(2) than by Eq.(1).

In Fig. 3a, very interesting results from [32] are shown. The authors presented test data of strained titanium in the $\sigma(d^{-1/2})$ coordinates. In the plot, two regions of the type (1) dependence can be distinguished. Namely, in a region of relatively large grain sizes, $k_y = 0.26$, while for grain sizes smaller than a certain critical grain size, $k_y = 1.59$. The cause of such a stepwise change in the coefficient k_y is not quite clear. Moreover, the authors note that for the second region, the term σ_0 has a negative value, which has no physical meaning, and that the value of the coefficient $k_y = 1.59 \text{ MPa}\cdot\text{m}^{1/2}$ seems to be overestimated and unrealistic.

A way out can be found if it is assumed that at a grain size $d_{cr1} \leq 1 \mu\text{m}$, the transition from dependence (1) to dependence (2) takes place. In Fig. 3b, the data shown in Fig. 3a are approximated with two intersecting curves in the coordinates of the

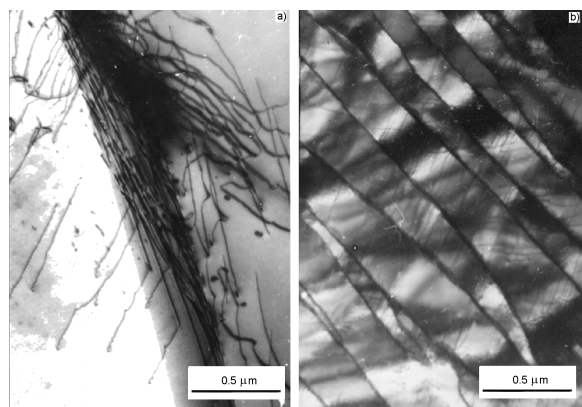


Fig. 4. Electron micrographs of polycrystalline molybdenum deformed at room temperature: ($\varepsilon \approx 2\%$ (a), $\varepsilon = 83\%$ (b)).

Hall-Petch equation. In this case, it is natural that dependence (2) has the form of an increasing curvilinear function.

Let us consider the physical meaning of such a transition. In the region of large grains of $d > d_{cr1}$ size, the ordinary Hall-Petch equation is satisfied. It is known that there are at least three models [7] explaining the existence of a type (1) dependence. The model of handover transfer, where the actuation of a dislocation source in a neighboring grain is initiated by stress concentration at the head of a dislocation cluster in the first grain, is most generally accepted. According to this model [4],

$$k_y = 2\sigma_n r^{1/2}, \quad (4)$$

where $\sigma_n = \alpha Gb/l$ is the stress of the source actuation in the neighboring grain (α being a coefficient of an order of 1; G , the shear modulus; b , the Burgers vector, l , the characteristic length of a Frank-Reed source); and r is the distance of the source from the head of the dislocation cluster.

In Fig. 4a, a typical structure illustrating the slip transfer through a grain boundary and obtained for a polycrystalline molybdenum sample after insignificant plastic deformation by rolling ($\varepsilon \approx 2\%$ at 20°C) is shown. Fig. 4b shows a structure obtained in the same material after a severe plastic deformation ($\varepsilon = 83\%$). It is important that within grains of the deformation origin, dislocations are hardly observed when their size becomes smaller than $0.4\ \mu\text{m}$.

Naturally, a certain distribution of sources in start stresses and distances (r) exists, but, in polycrystalline materials, these values become averaged, so $k_y = \text{const}$

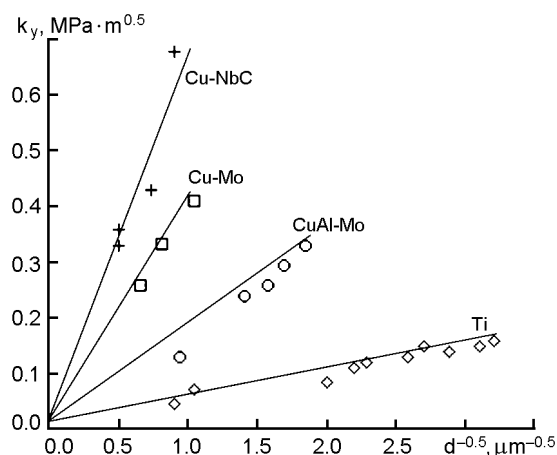


Fig. 5. Dependences of k_y on the grain size [25].

in the grain size range where Eq.(1) is satisfied. The coefficient k_y appears to be sensitive to blocking of dislocations due to impurities and may vary rather substantially depending on the impurity content, heat treatment, and, in some cases, at changes in the grain size [7].

In [25], attention was given to the fact that when the grain size decreases to values close in the order to r and l ones, these values are no longer constant and, since their size cannot be larger than d , we can assume that as the grain size decreases to values smaller than d_{cr1} , the r and l ones are proportional to d . Then it is easy to obtain from expression (4) that, in this case (for $d < d_{cr1}$), the k_y value also depends on the grain size as follows:

$$k_y = \alpha_1 Gb/d^{1/2} = k_1/d^{1/2}. \quad (5)$$

It is just this $k_y(d)$ dependence that was obtained in [25] for a number of microcrystalline materials in the corresponding grain size range (Fig. 5).

Thus, strictly speaking, the dependences (1) and (2) are equivalent in the sense that both dependences reflect the handover character of slip transfer through a grain boundary. Only at $d > d_{cr1}$, the coefficient k_y is constant, while at $d < d_{cr1}$, it becomes dependent on the grain size according to expression (5). Correspondingly, substituting expression (5) in formula (1), we obtain dependence (2).

In [18, 32], the following problem was also discussed. As the grain size decreases, the possible number of dislocations in a flat cluster and, therefore, the stress concentration at the head of such a cluster must diminish. Then, for a source in a neighbouring grain to be actuated, the stresses must

increase, that is what defines the cause of yield stress rise according to expression (1). It is clear, however, that there exists a grain size at which no clusters are formed within the grain, and the yield stress must be proportional to the activation stress of the Frank-Reed source, i.e.,

$$\sigma_y = \sigma_0 + \alpha_1 Gb/d. \quad (6)$$

Actually, in [33], such a stress necessary for the deformation of severely deformed iron has been determined and it has been shown that $\alpha_1 = 3.4-5.9$. Since the Frank-Reed source characteristic length l must be equal to a certain part of the grain size d in order that the source can work (it is usually assumed that $l \geq 1/3d$), the presented estimation of α_1 seems to be realistic.

In conclusion of this section, we can note what follows. The transition from dependence (1) to (2) takes place not only in the case of grain refinement by methods of severe and intense deformations, but also in polycrystalline materials where the grain size is varied using other technologies, in particular, when such microcrystalline materials are obtained by gas-phase deposition [23-25, 34]. As the critical grain size d_{cr1} is attained, essentially no dislocation clusters are nucleated inside such fine grains, which is confirmed by electron microscopy studies.

It is clear, however, that, as the grain size further decreases, there comes a moment when, for a dislocation source to be actuated within a grain, a stress of the order of the theoretical shear strength is required. Thus, the mechanism of handover slip transfer must be exhausted, and the yield stress must attain the theoretical strength. This, however, does not occur. Moreover, in many cases, the yield stress drops abruptly. In what follows, the causes of such a behavior are discussed.

2. Yield strength of polycrystals in a nanometer grain size range. In Fig. 6, presented is a dependence of the normalized yield stress $(\sigma - \sigma_0)/k$ on the size of nanograins (to a grain size of about 2 nm) for some materials that was generalized in [14]. It is seen that in some cases, in a grain size range smaller than a certain characteristic critical size d_{cr2} (as a rule, 10-30 nm), a further grain refinement, in contradiction to relation (1), either does not result in hardening or is accompanied by softening (the inverse Hall-Petch effect).

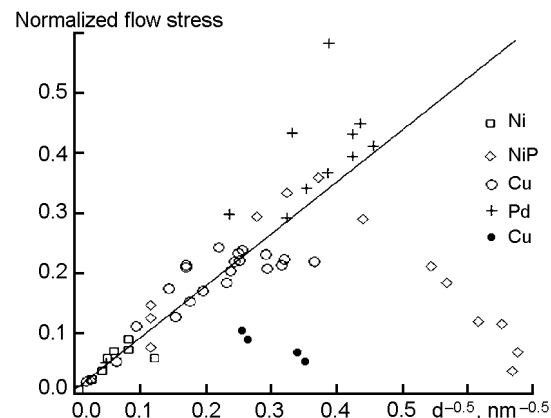


Fig. 6. Dependences of the normalized yield stress on the grain size for some materials [14].

At present, numerous works are known devoted to the discussion of similar deviations [11-18, etc.]. It is assumed that the plastic straining mechanisms in materials with nanograins differ from those in the coarse-grained analogs, which is connected with both the small size of structural elements and an increase in the volume fraction of the so-called "imperfect" material, namely, grain interfaces. For the description of obtained experimental results, a numerous theoretical models were proposed for plastic straining in nanocrystalline materials.

A general classification of such models is presented in [18]. It includes models describing the yield strength of a nanocrystalline material basing on different "mixture rules", models where ordinary motion mechanisms of lattice dislocations dominate, models of grain-boundary plasticity mechanisms (grain-boundary slip, diffusion plasticity along grain boundaries), models of twinning mechanisms. Some models take into account the competition of different straining mechanisms, because, as a rule, several mechanisms act simultaneously in real materials.

In our opinion, among all the above-mentioned models, the most thoroughly developed are those basing on mixture rules and the concept of a nanocrystalline material in the form of a two-phase composite consisting of an intragranular and an intergranular phases. Such an approach can be used both without concretizing the plastic straining mechanisms of crystallites and intergranular boundaries and taking those into account. At the same time, the dislocation models that assume the presence of plastic flow carriers in the form of lattice and

grain-boundary dislocations, joint disclinations, are considered to be rather problematic because direct investigations indicate that dislocations are absent in nanograins. Nevertheless, the authors of all proposed models noted that they agree well with experimental results.

However, along with experimental data testifying to the presence of the inverse Hall-Petch effect in the nanometer grain size range, there exist data on an increase in the strength (hardness) in the same grain size range, e.g., results presented in [35]. A dependence of the yield strength on the grain size d in deposited chromium (Fig. 2) obtained by the authors indicates also an abrupt increase in the yield strength at a grain size smaller than $d_{cr2} \approx 0.1 \mu\text{m}$ and can be described by the relation $\sigma = \sigma_0 + k_3 d^{-3}$.

According to the concept of "useful" impurities proposed by the authors [24], the observed drastic strength (hardness) increase of nanocrystalline chromium is due to the influence of interstitial oxygen atoms, which are "useful" impurities for chromium because they exhibit a stronger chemical bond with chromium atoms than that between chromium atoms. The segregation of oxygen results in the formation of a stronger (harder) shell from interfaces, which forms a honeycomb structure with softer plastic chromium grains being located within it (Fig. 7).

It should be noted that an abrupt yield strength rise as a result of the grain refinement to a size smaller than d_{cr2} is possible only in multicomponent systems at an appropriate choice of components. In single-component materials, a decrease in the grain size results in an increased volume fraction of imperfect material in grain boundaries and at triple grain-boundary junctions and, therefore, to a decreased yield strength (hardness).

To describe the yield stress in a nanometer grain size range, we used the approach based on a mixture rule. We assumed that the volume fraction of a crystalline material is $(d - t/d)^2$, the fraction of grain boundaries is $(1 - (d - t/d)^2)$. The yield stress value of a material at grain refinement depends on the strength of their boundaries (it increases as grain boundaries are strengthened by useful impurities and decreases in single-component materials). Taking into account the shear occurs in a plane, we propose the following relation for the yield stress at a grain size smaller than d_{cr2} :

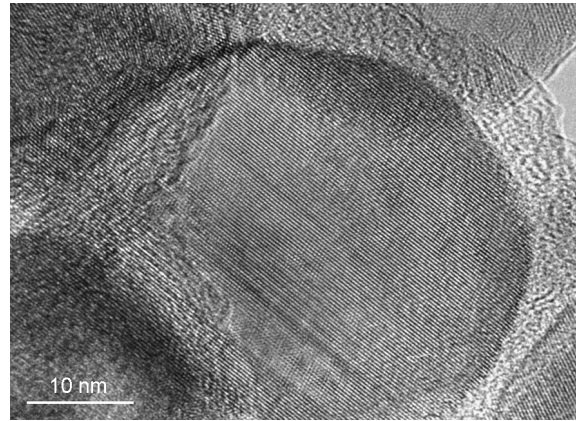


Fig. 7. Electron high-resolution micrograph of chromium deposited using a magnetron technology [24].

$$\sigma_3 = \left(1 - \left(\frac{d-t}{d}\right)^2\right) \sigma_B + \left(\frac{d-t}{d}\right)^2 \sigma_{CR}, \quad (7)$$

where t is the thickness of grain boundaries, σ_B , the strength of grain boundaries; and σ_{CR} , the grain theoretical strength.

Since the strength of dislocation-free grains tends to the highest possible (theoretical) strength of a material, σ_{CR} can be assumed to correspond to the theoretical strength of the material. For instance, it is stated [36] that there exists a certain critical crystallite size at which conventional mechanisms of plasticity and hardening stop acting and an ideal strength is realized in grains, at which the microhardness no longer depends on the grain size and remains constant. For a number of metals, the values of such critical grain size evaluated in [36] show a large spread. For example, this size ranges from 1.2 to 59.3 nm for aluminum and from 1.7 to 39.4 nm for copper.

It is worthy to note that, when refining intergranular straining mechanisms of a material in a nanometer grain size range, we can represent σ_B in expression (7) in an analytic form.

3. Generalized Hall-Petch equation. Thus, the consideration of the yield strength variations in a wide grain size range, including the nanometer range, indicates the presence of two critical sizes that define changes in the straining mechanism when being attained. When the grain is refined to d_{cr1} , the yield strength variation character is described by the Hall-Petch relation (1), in the grain size interval from d_{cr1} to d_{cr2} , it is described by Eq.(2), and at grain sizes smaller than d_{cr2} , by relationship (7).

One can combine the indicated dependences and derive a generalized equation that describes the yield strength variation depending on the grain size in a wide range with regard to transitions to different dependences at attaining the critical sizes, using the so-called sigma functions, namely, S-functions [37]. A feature of S-functions (the Gompertz function, Pearl function, etc.) is that in the vicinity of the critical argument, their value changes from 0 to 1, that is why their use enables one to combine functions $f_1(x)$ and $f_2(x)$ having the plots intersecting at certain critical values, in one common function:

$$F(x) = S(x)f_1(x) + (1 - S(x))f_2(x). \quad (8)$$

The chosen S-function must correspond to the physical meaning of transitions at attaining the critical values. Since it is known that in the material, there exists a certain grain-size distribution described by the log-normal distribution

$$f(d) = \frac{A}{s_{1,2}d\sqrt{2\pi}} \exp\left(-\frac{\ln(d) - \ln(d_{cr1,cr2})}{2s_{1,2}^2}\right), \quad (9)$$

where $A = 1 = const$ and $s_{1,2}$ is the distribution variance for the first and second transition, respectively, then, to construct a generalized equation, it is expedient to use antiderivative (9) as an S-function

$$S(d) = -\int f(d)d(d) = \frac{1}{2} + \frac{1}{2} \operatorname{erf}\left(\frac{\ln(d) - \ln(d_{cr})}{s\sqrt{2}}\right), \quad (10)$$

where $\operatorname{erf}(x) = \frac{2}{\sqrt{\pi}} \int \exp(-t^2)dt$, $t = 0 \dots x$.

An equation constructed using S-functions chosen in such a way is a generalization of Eqs.(3), (4), and (5) and has the form

$$\sigma = \{\sigma_1 S_1(d_{cr1}) + \sigma_2 (1 - S_1(d_{cr1}))\} S_2(d_{cr2}) + \sigma_3 (d)(1 - S_2(d_{cr2})). \quad (11)$$

According to (11), if all grains corresponding to the given distribution are in the range of values above d_{cr1} , then the Hall-Petch dependence (1) holds, for grain sizes lying in the interval from d_{cr1} to d_{cr2} , dependence (2) is valid, and for grain sizes smaller than d_{cr2} , dependence (7) holds. From (11), it also follows that at grain sizes smaller than d_{cr2} , the yield strength may increase or decrease depending on the strength of grain boundaries. Figure 8a

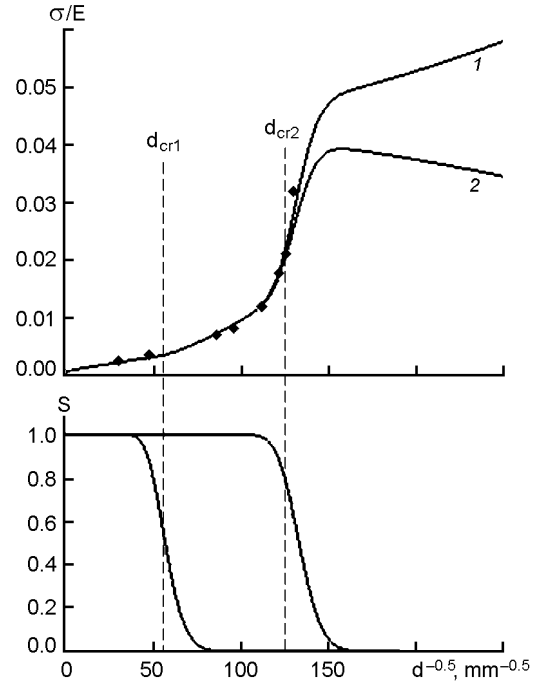


Fig. 8. Dependences of the normalized yield strength on the grain size for deposited chromium in the case of "strong" boundaries (curve 1) and "weak" boundaries (curve 2) (a) and S-functions in the vicinity of critical grain sizes (b).

shows a dependence of the normalized yield strength (the yield strength divided by Young's modulus) on the grain size, constructed for a wide grain size range according to (11) and with account for the following experimentally obtained data for deposited chromium: $\sigma_0 = 0.22$ GPa, $k_y = 1.4$ kg/mm^{3/2}, $d_{cr1} = 0.31$ μ m, $d_{cr2} = 0.057$ μ m, $s_1 = 0.3$, and $s_2 = 0.15$. In the nanosize range, the value $\sigma_{CR} = 12$ GPa is taken, which is somewhat higher than the lowest imate of the chromium theoretical strength, and the thickness of grain boundaries is $t = 2$ nm. In the case of a strong bond along grain boundaries ("strong" boundaries), at $\sigma_{B1} = 20$ GPa ($\sigma_{B1} > \sigma_{CR}$), an abrupt increase in the yield strength (curve 1) corresponds to the transition to nanosizes, which agrees well with an experimental curve (Fig. 2). In the hypothetical case of weak intergranular cohesion ("weak" boundaries), we take $\sigma_{B2} = 2$ GPa (σ_{B1} is much smaller than σ_{CR}) and observe its decrease (curve 2), i.e., the so-called inverse Hall-Petch relation.

Thus, it is seen that Eq.(11) takes into account the hardening mechanism changes

in the vicinity of the critical grain sizes and agrees well with the experimental data obtained by the authors. However, it should be noted that the plasticity mechanism of nanostructured materials for grain sizes that rules out the intragranular straining can be further refined, and, in this case, σ_3 will take a more specific form.

In view of the fact that, in Fig. 8a, the yield strength normalized with respect to Young's modulus is laid off on the ordinate axis, we consider that the obtained dependence can be used in the future for a comparative analysis of the hardening level not only for chromium, but also for other materials. However, since Young's modulus of nanostructured materials may differ substantially from tabular values (due to the state of grain boundaries, texture, and other factors), it is reasonable to obtain a dependence of the normalized hardness on the grain size. This seems to be convenient because, in many cases, using the method of automatic indentation (nanoindentation), it is rather easy to determine both the hardness and Young's modulus values and, hence, their ratio, in one experiment at each point at which the hardness is tested.

We can pass from the $\sigma/E(d)$ dependence to $H/E(d)$ one using the Marsh formula that relates the hardness and the yield stress:

$$\frac{HV}{\sigma_s} = 0.6 \ln \frac{E}{\sigma_s} + 0.28 + 0.6 \ln \frac{3}{4 + \nu}, \quad (12)$$

where E is Young's modulus and ν is Poisson's ratio.

In Fig. 9, the dependence of the hardness normalized with respect to Young's modulus on the grain size is presented (the hardness values of the grain-boundary material are indicated near the curves) calculated in the mentioned way. This dependence enables us to describe both the descending branch for the case of "weak" boundaries and the stabilization or even increase in the strength (hardness) in the case of "strong" boundaries in the nanometer grain size range.

The dependence $H/E(d)$ can be also used for the fast evaluation of a material hardening degree by comparing it with the theoretical hardness value of the material and hence with the theoretical hardness value of the material which corresponds of the highest possible hardening value for the given material and, hence, with the largest possible value of the $H/E = H_{theor.}/E$ ratio.

The concept of theoretical hardness was introduced by the authors in [38]. The theo-

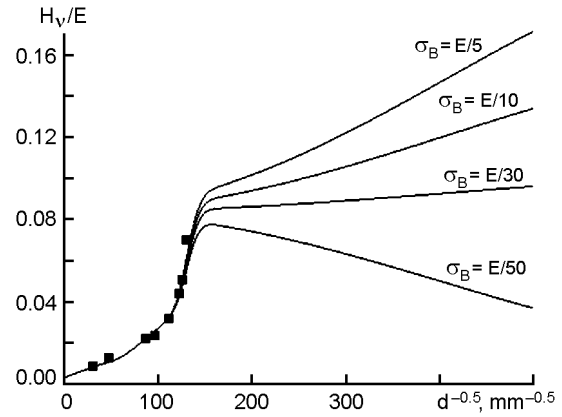


Fig. 9. Dependences of the hardness normalized with respect to Young's modulus on the grain size for some values of a grain-boundary material strength.

retical hardness of a material is its maximal hardness which can be attained provided that the stress that causes plastic flow in the material under the indenter corresponds to the theoretical shear strength of this material. The theoretical hardness value can be calculated using the formula

$$H_{theor.} = \beta E / \alpha (1 + \nu), \quad (13)$$

where ν is Poisson's ratio, the α values are within limits $5 \ll \alpha \ll 30$; for metallic materials, we can take $C \approx 3$.

It is seen that for the value $\alpha = 30$, the theoretical hardness can be $H_{theor.} \approx 0.1 E$ depending on Poisson's ratio of the material. These values are the lower limit of the possible theoretical hardness.

It was noted [39, 40], that, when the indentation is done using a Berkovich indenter, the ratio of the hardness to the elasticity modulus is described as

$$H/E^* = 0.3206 \cdot (h_s/h_c), \quad (14)$$

where h_c is the penetration depth within which the indenter contacts with a material after complete loading up to P_{max} ; h_s , the part of the indenter penetration depth within which the contact with the material is absent as a result of a sink-in formed in the material near the indenter; and E^* , the effective Young's modulus ($E^* = E/(1 - \nu^2)$), where ν is Poisson's ratio and E is Young's modulus.

An experimentally obtained dependence H/E^* on (h_s/h_c) (Fig. 10) shows that, at indentation with a Berkovich indenter, for a material with the given elasticity modulus,

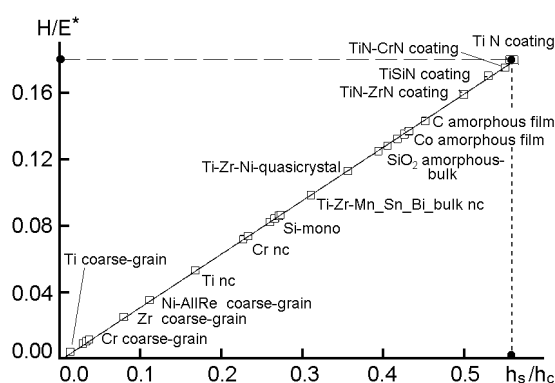


Fig. 10. Experimental dependence of H/E^* ratio on the ratio of the characteristics h_s/h_c obtained at indentation [39–40].

the ratio H/E^* cannot exceed 0.1803, and the largest specific hardness values ($H/E^* \approx 0.14\text{--}0.15$) correspond to the amorphous or amorphous-nanocrystalline (quasi-crystalline) states.

To conclude, at decreasing the grain size (or the size of another structural element, e.g., the layer thickness in layered materials), three characteristic regions with qualitatively different influence of the structure on the yield stress can be distinguished that are separated by two critical grain sizes. Respectively, at least three analytical dependences of the yield stress for each region can be considered. The first two regions are characterized by handover slip transfer through grain boundaries with a constant coefficient of the Hall-Petch equation in the first region ($k_y = \text{const}$) and with a coefficient of the Hall-Petch equation depending on the grain size ($k_y = k_1/d^{1/2}$) in the second one. This results in a change of the exponent in the Hall-Petch equation from $-1/2$ to -1 as the grain size decreases to a value below d_{cr1} . When passing to the nanosize region through d_{cr2} , the dependence of the yield stress on the grain size can be described using a composite model.

To construct a generalized dependence of the yield stress on the grain size, it has been proposed to use S-functions, for which antiderivatives of log-normal grain-size distributions have been chosen. A generalized dependence of the yield stress on the grain size normalized with respect to Young's modulus, which describes both the "negative" Hall-Petch relation (for "weak" boundaries) and the increasing dependence (for "strong boundaries"). Using the Marsh formula, a generalized dependence of the hardness normalized with respect to Young's modulus on the grain size was ob-

tained, which makes it possible to use the automatic indentation method to assess the structural sensitivity of hardening in a wide variation range of the structural element sizes. A further refinement of the proposed technique must be connected with the refinement of the plasticity mechanism in the third stage and, hence, the analytical dependence of the yield stress in the region of nanocrystalline and amorphous-nanocrystalline structures.

References

1. L.S.Palatnik, A.I.Il'inskii, *Usp. Fiz. Nauk*, **95**, 613 (1968).
2. E.O.Hall, *Proc. Phys. Soc. B*, **64**, 74 (1951).
3. N.J.Petch, *J. Iron Steel Inst.*, **174**, 25 (1953).
4. A.H.Cottrell, *Structure and Mechanical Properties of Metals*, Metallurgiya, Moscow (1967) [in Russian].
5. R.V.Armstrong, *Ultrafine Grains in Metals*, Metallurgiya, Moscow (1973) [in Russian].
6. H.Conrad, *Ultrafine Grains in Metals*, Metallurgiya, Moscow (1973) [in Russian].
7. V.I.Trefilov, Yu.I.Milman, S.A.Firstov, *Physical Fundamentals of Strength of Refractory Metals*, Naukova Dumka, Kiev (1975) [in Russian].
8. A.M.Thompson, *Met. Trans.*, **8**, 833 (1977).
9. V.I.Trefilov, V.F.Moiseev, E.P.Pechkovskii et al., *Strain Hardening and Fracture of Polycrystalline Metals*, Naukova Dumka, Kiev (1987) [in Russian].
10. N.A.Graivoronskii, G.F.Sarzhn, S.A.Firstov, *Metallofiz. Noveish. Tekhnol.*, **19**, 2 (1997).
11. R.A.Andrievskii, A.M.Glezer, *Fiz. Met. Metalloved.*, **89**, 91 (2000).
12. H.Gleiter, *Progress Mater. Sci.*, **33**, 223 (1989).
13. H.Gleiter, *Nanostruct. Mater.*, **1**, 1 (1992).
14. R.A.Masumura, P.M.Hazzledine, C.S.Pande, *Acta Mater.*, **46**, 4527 (1998).
15. V.G.Gryaznov, L.I.Trusov, *Progress Mater. Sci.*, **37**, 289 (1993).
16. R.W.Siegel, *J. Phys. Chem. Solids*, **55**, 1097 (1994).
17. G.Palumbo, U.Erb, K.T.Aust, *Scr. Met. Mater.*, **24**, 2347 (1990).
18. M.Yu.Gutkin, I.A.Ovidko, *Physical Mechanics of Deformable Structures, Vol.1: Nanocrystalline Materials*, Institute for Problems of Machine Building, Saint Petersburg (2003) [in Russian].
19. U.F.Kocks, *Metal. Trans.*, **1**, 1121 (1970).
20. V.G.Gryaznov, M.Yu.Gutkin, A.E.Romanov, L.I.Trusov, *J. Mater. Sci.*, **28**, 4359 (1993).
21. H.S.Kim, Y.Estrin, M.B.Bush, *Acta Mater.*, **48**, 493 (2000).
22. S.Takeuchi, *Scr. Mater.*, **44**, 1483 (2001).
23. S.A.Firstov, T.G.Rogul, V.T.Marushko, V.A.Sagaydak, *Vopr. Materialoved.*, **33**, 201 (2003).

24. S.A.Firstov, T.G.Rogul, V.L.Svechnikov et al., *Metallofiz. Noveish. Tekhnol.*, **25**, 1153 (2003).
25. S.A.Firstov, Yu.F.Lugovskoi, *Elektron. Mikroscop. Prochn. Mater.*, Issue 15, 83 (2008).
26. S.Veprek, *J. Vac. Sci. Technol.*, **17**, 2401 (1999).
27. V.A.Manilov, V.G.Tkachenko, V.I.Trefilov, S.A.Firstov, *Izv. Akad. Nauk SSSR, Metally*, No.2, 114 (1967).
28. R.Z.Valiev, I.V.Aleksandrov, Nanostructured Materials Obtained by Intensive Plastic Deformation, Logos, Moscow (2000) [in Russian].
29. V.V.Rybin, Large Plastic Deformations and Fracture of Metals, Metallurgiya, Moscow (1986) [in Russian].
30. A.I.Ilinskii, Structure and Strength of Layered Dispersion-Strengthened Films, Metallurgiya, Moscow (1984) [in Russian].
31. J.Gil Sevellano, P.van Houtte, E.Aernoudt, *Progress Mater. Sci.*, **25**, 69 (1981).
32. A.V.Nokhrin, V.N.Chuvildeev, E.S.Smirnova et al., Mechanical Properties of Nanocrystalline and Microcrystalline Metals, Federal Agency of Education of the Russian Federation, Lobachevsky State Univ. of Nizhny Novgorod, Nizhny Novgorod (2007) [in Russian].
33. G.Langford, M.Cohen, *Trans. Amer. Soc. Met.*, **62**, 623 (1969).
34. B.A.Movchan, *Avtomat. Svarka*, No.11, 166 (2008).
35. D.Vollath, D.V.Szabo, *Nanostruct. Matter.*, **4**, 927 (1994).
36. N.Wang, Z.Wang, K.T.Aust, U.Erb, *Acta Metall. Mater.*, **43**, 519 (1995).
37. S.A.Firstov, T.G.Rogul, O.A.Shut, *Fiz. Khim. Mekh. Mater.*, No.6, 7 (2009).
38. S.A.Firstov, T.G.Rogul, *Dop. Nats. Akad. Nauk Ukr.*, No.4, 110 (2007).
39. S.A.Firstov, E.P.Pechkovskii, V.F.Gorban et al., *Dop. Nats. Akad. Nauk Ukr.*, No.12, 100 (2007).
40. S.A.Firstov, T.G.Rogul, V.F.Gorban et al., in: Key Engineering Materials (2009), v.409, p.128.

Перехід від мікро- до наноструктур, граничне зміцнення

С.О.Фірстов, Т.Г.Розуль, О.О.Шут

Обговорюються закономірності зміни залежності напруги плинності при переході від мікро- до наноструктурованого стану. Показано, що за допомогою S-функцій можна отримати узагальнене рівняння залежності границі плинності від розміру зерна з урахуванням зміни механізмів зміцнення полікристалів в околі критичних розмірів зерен $d_{кр1}$ і $d_{кр2}$. Це рівняння дозволяє описати як ефекти знеміцнення при переході до наноструктур (так званий "негативний" хід залежності Холла-Петча), так і, навпаки, різке зміцнення за умови підвищеної міцності межзеренного зчеплення.