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Modification of the Hall-Petch relationship for submicron-grained fcc metals

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ABSTRACT

Experimental data show that the conventional Hall-Petch relationship cannot be maintained in its original form for metals having submicrometer structures. We now propose a dislocation model which modifies the Hall-Patch relationship to provide a uniform description of the grain size strengthening of submicron-structured face-centered cubic (f.c.c.) metals and solid solution alloys.

1. Introduction

It was a significant development in materials science when, approximately seventy years ago, in 1951 Eric Hall [1] and in 1953 Norman Petch [2] published the relationship now known as the Hall-Petch equation:

$$\sigma_y = \sigma_0 + A \bullet d^{-1/2} \tag{1}$$

where this relationship demonstrates that the yield stress, σ_y, necessary for yielding and plastic deformation of polycrystalline materials changes linearly with the reciprocal of the square root of the grain size, d. In Eq. (1), σ_0 is the friction stress (or yield stress of a single crystal) and A is a positive material constant. This equation, which has become one of the most cited in materials science, demonstrates the basic strengthening mechanism in polycrystalline materials, as the yield stress and then the strength increase with decreasing grain size.

This relationship soon became a driving force of several efforts to obtain finer grain sizes in conventional materials [3–11]. Thus, through various severe plastic deformation (SPD) processes [4–11] in bulk crystalline materials, average grain sizes in the sub-micrometer ($d <$ 1000 nm) range were achieved and this significantly increased the strength of these ultrafine-grained materials.

In practice it is important to note that both Hall and Petch developed Eq. (1) phenomenologically, basing their conclusions on experimental data obtained on samples of iron, copper and brass [1–3]. This relationship is well established for polycrystalline metals and alloys having average grain sizes of $d > 1$ μm, but more recent studies show that the relationship no longer holds in the range of sub-micron and exceptionally small grain sizes. On the one hand the parameter A in Eq. (1) paradoxically decreases in the submicron range [12–14] and on the other hand at grain sizes below approximately 20 nm the Hall-Petch equation is no longer valid since, as the grain size decreases, the yield strength also decreases and the material becomes softer [11,12,14]. This latter behavior is also called the inverse Hall-Petch effect and it has been explained using several different interpretive models [15–17].

The present work is focused on experimental data obtained from submicron-structured materials having grain sizes in the range between 100 and 1000 nm. Our main motivation is to present a dislocation model that provides an appropriate modification of the Hall-Petch relation and produces a uniform description of the large numbers of results now available in the literature for submicron-structured solid solution face-centered cubic (f.c.c.) metals and alloys.

2. Modification of the original Hall-Petch relationship

a) Physical background of the original Hall-Petch equation

When a polycrystalline specimen is subjected to a gradually increasing load, the critical shear stress is first reached in the slip plane having the most favorable orientation in any selected grain. If there is a Frank-Read source, S, belonging to this slip system, it will emit a series of dislocations as shown schematically in grain A of Fig. 1a. As a result of increasing external forces, the source emits an increasing number of dislocations which then pile up at the grain boundary (GB) as shown in Fig. 1b. In the stress field of the pile-ups, a maximum tensile stress, σ_{pile}, forms in the adjacent grain with a magnitude given by Ref. [18]:

$$\sigma_{pile} = n \bullet \tau_e \tag{2}$$

where τ_e is the effective shear stress operating in the slip plane belonging to the source and n is the number of dislocations in the pile-up. At a given value of τ_e, due to the back stress of the piled-up dislocations, the operation of the source is halted after the emission of n dislocations determined by Ref. [18]:

$$n = \frac{\pi(1-v)d}{\mu b}\tau_e \tag{3}$$

where v is Poisson's number, μ is the shear modulus, b is the magnitude of the Burgers vector and $d/2$ is the size of the pile-up set which can be identified, in the present case, with one-half of the average grain size. From equations (2) and (3):

$$\sigma_{pile} = \frac{\pi(1-v)d}{\mu b}\tau_e^2 \tag{4}$$

This stress may activate multiple slip in grain B (Fig. 1a) after reaching a critical value. The initiation of the macroscopic deformation is related to the value of σ, the external stress, when σ_{pile} reaches a critical value necessary to initiate multiple slip. Considering also Schmid's law, the average critical shear stress acting in each grain, τ_e, is proportional to σ and the yield stress, σ_y based on Eq. (4) can be given as

$$\sigma_y = \sigma_o + K \bullet d^{-1/2} \tag{5}$$

where K is the constant containing the parameters in Eq. (4) as well as the Schmid factor and σ_o is the yield strength of the single crystal. This is the physical background of the Hall-Petch relationship which is basically interpreted by the concept of dislocation pile-ups formed at grain boundaries [11,14]
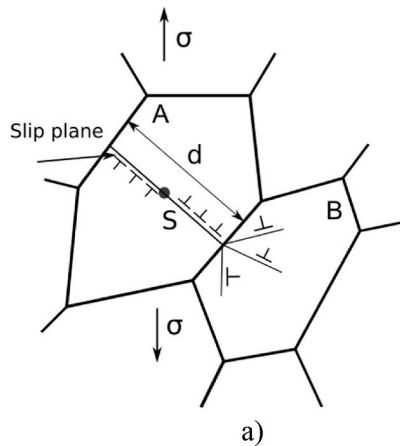
b) Modification of the Hall-Petch equation

Let us consider again Eq. (4). It follows that normalizing the stresses by the shear modulus and the grain size by the magnitude of the Burgers vector leads to:

$$\frac{\sigma_{pile}}{\mu} = \pi(1-v)\left(\frac{d}{b}\right)\left(\frac{\tau_e}{\mu}\right)^2 \tag{6}$$

Given that Poisson's number is almost the same for all f. c.c metals ($v \approx 1/3$), the dimensionless relationship in Eq. (6) is already appropriate for a unified description of the properties of different f. c.c metals.

For large grains, it may be assumed that macroscopic plastic deformation is observed if the normalized stress, σ_{pile}/μ, reaches a constant value K_1 to initiate multiple slip, for which the normalized effective shear stress is then given by

$$\frac{\tau_e}{\mu} = \sqrt{\frac{K_1}{\pi(1-v)}} \bullet \left(\frac{d}{b}\right)^{-\frac{1}{2}}. \tag{7}$$

This corresponds to the conventional Hall-Petch relationship for normalized stress with an exponent of $-1/2$ associated with the normalized grain size.

Alternatively, for very small grain sizes ($d < 100$ nm), the average number of dislocations in the pile-up tends to one, or to a small constant number K_2, giving pile-ups breakdown [11,14]. In the absence of a dislocation pile-up, replacing the value of n in Eq. (3) as constant K_2, the normalized stress then can be expressed as

$$\frac{\tau_e}{\mu} = \frac{K_2}{\pi(1-v)}\left(\frac{d}{b}\right)^{-1} \tag{8}$$

where the normalized effective shear stress, $\left(\frac{\tau_e}{\mu}\right)$, is directly proportional to the reciprocal of the normalized grain size, $\left(\frac{d}{b}\right)^{-1}$. Thus, the exponent of the normalized grain size changes from $-1/2$ to -1 when there is a transition from large to small grain size ranges.

Since experimental experience [11,14] shows that in a wide grain size range the grain size exponent usually shows a continuously decreasing trend in the Hall-Petch relationship with decreasing grain size, it is reasonable to assume that the normalized effective shear stress is directly proportional to the power of the normalized grain size so that

$$\frac{\tau_e}{\mu} = K_3 \bullet \left(\frac{d}{b}\right)^{\beta} \tag{9}$$

where K_3 and β are constants depending on the grain size range. Thus,
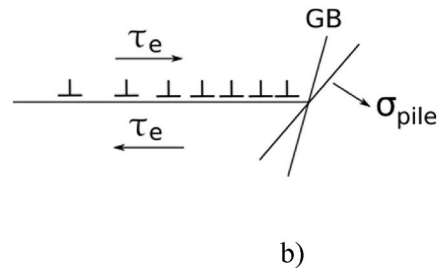
Fig. 1. Effect of grain size on the yield stress: a) Schematic of the operation of a Frank-Read source (S) in a selected grain (A) and b) Effect of the corresponding set of pile-up of dislocations at the grain boundary (GB).

for large grain sizes $d > 1000\,nm$, $K_3 = \sqrt{\frac{K_1}{\pi(1-v)}}$ and $\beta = -1/2$ (see Eq. (7)), whereas for small grain sizes $d < 100\,nm$, $K_3 = \frac{K_2}{\pi(1-v)}$ and $\beta = -1$ (see Eq. (8)). For the intermediate submicron-size range, the value of the exponent β lies between $-1/2$ and -1.

Considering again Schmid's law, as well as taking into account also the yield stress, σ_o, of the single crystal, the conventional Hall-Petch relationship is now modified to the form

$$\frac{\sigma}{\mu} = \frac{\sigma_0}{\mu} + A^* \bullet \left(\frac{d}{b}\right)^{\beta} \tag{10}$$

where A^* is a constant depending on the grain size range and the value of the exponent β is determined by using experimental data.

3. Verification of the proposed model and its application to experimental data

The application of Eq. (10) to experimental data may be examined using data from several ultrafine-grained fcc metals such as Al [5, 19–22], Au [23,24], Cu [25,26] and Ni [27–30] as well as solid solution Al-1wt%Mg and Al-3wt%Mg alloys [5] having an average grain size, d, in the range between 100 and 1300 nm. For the purpose of the analysis, it is worthwhile examining the data in a double logarithmic representation as shown in Fig. 2. It should be noted that, for a given material, the σ_o term is usually much smaller than the yield stress of the ultrafine-grains. For example, for pure Cu σ_o is less than 30 MPa and σ is greater than 380 MPa [31]. For this reason, to a first approximation, and with an error of less than 10%, the normalized stress (σ/μ) can be considered proportional to the power of the normalized grain size (d/b). Thus, a straight line can be fitted approximately to the $\ln\left(\frac{\sigma}{\mu}\right) - \ln\left(\frac{d}{b}\right)$ data and the slope gives, approximately, the value of the exponent β. It is readily apparent from Fig. 2 that the experimental data fit a straight line having a slope of about $-3/4$.

Based on this analysis, Fig. 3 shows directly the normalized yield stress, σ/μ, as a function of the normalized grain size, d/b, with a best-fitted line based on Eq. (10). This best fitting is obtained when $\frac{\sigma_0}{\mu} = 0.0008 \pm 0.0002$, $A^* = 2.22 \pm 0.15$ and $\beta = -0.75 \pm 0.04$. The analysis shows clearly that the strength of ultrafine-grained fcc metals and solid solutions can be uniformly described by an appropriate modification of the Hall-Petch relationship of the form
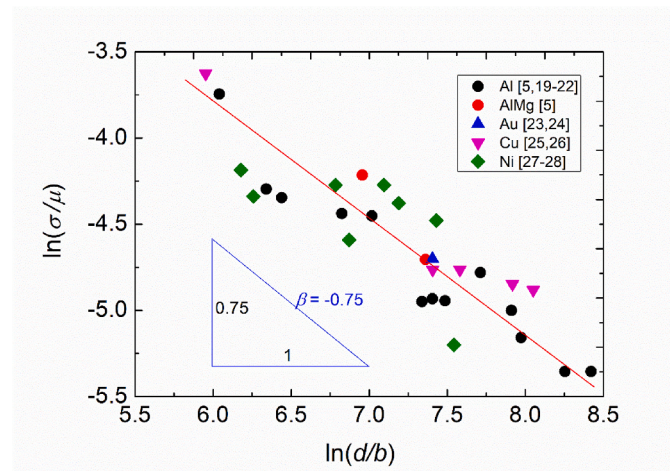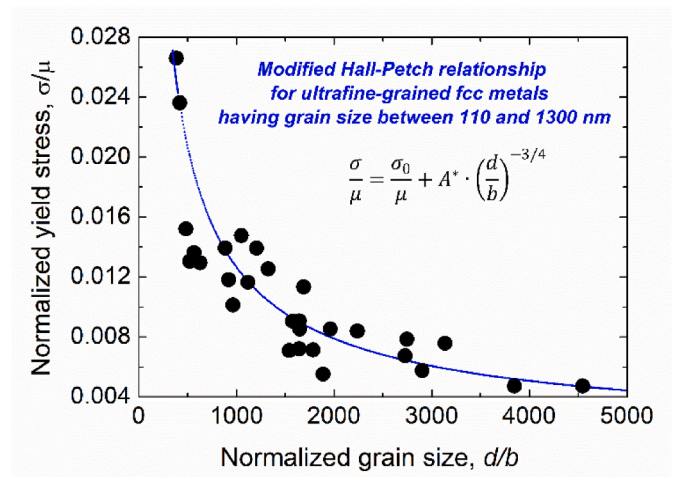

Fig. 3. Direct presentation of the normalized yield stress-normalized grain size relationship, proposing a modification of the Hall-Petch relationship for ultrafine-grained fcc metals and solid solutions.

$$\frac{\sigma}{\mu} = \frac{\sigma_0}{\mu} + A^* \bullet \left(\frac{d}{b}\right)^{-3/4} \tag{11}$$

The fact that several ultrafine-grained metals and alloys behave according to this modified Hall-Petch relationship is indicative of the robustness of the applicability of the model and the underlying physical phenomenon. Based on Eq. (11) with the parameters given above, the strength of any sub-micron structured fcc metal or solid solution may be estimated if the grain-size is known. It should be noted that the conventional Hall-Petch behavior (for $d > 1000\,nm$, $\beta = -1/2$) is the consequence of the activation of multiple slip within the individual grains. In the case of single slip ($d < 100\,nm$), $\beta = -1$. In the middle range, the value of $-3/4$ for β is certainly representing an intermediate state in the slip-system.

In summary, an appropriate modification of the original Hall-Petch relationship is proposed in order to maintain its applicability for submicron-structured fcc metals and solid solution alloys. It is demonstrated that the proposed relationship works well for a uniform description of a large number of results in the literature thereby demonstrating the overall robustness of the applicability of this model. In addition, and as an important consequence, the modified Hall-Petch relationship permits an estimation of the strength of any sub-micron structured fcc metal or solid solution when the grain-size is known.

Originality statement

I write on behalf of myself and all co-authors to confirm that the results reported in the manuscript are original and neither the entire work, nor any of its parts have been previously published. The authors confirm that the article has not been submitted to peer review, nor has been accepted for publishing in another journal. The author(s) confirms that the research in their work is original, and that all the data given in the article are real and authentic. If necessary, the article can be recalled, and errors corrected.

CRediT authorship contribution statement

Nguyen Q. Chinh: Conceptualization, Formal analysis, Writing – original draft, Writing – review & editing. **Dániel Olasz:** Conceptualization, Formal analysis, Writing – original draft, Investigation, Data curation. **Anwar Q. Ahmed:** Investigation, Data curation. **György Sáfrán:** Investigation, Data curation. **János Lendvai:** Conceptualization, Formal analysis, Writing – original draft. **Terence G. Langdon:**

Fig. 2. Characterization of the relationship between normalized yield stress and normalized grain size in a double-logarithmic $\left(\ln\frac{\sigma}{\mu} - \ln\frac{d}{b}\right)$ representation for ultrafine-grained fcc metals and solid solution alloys.

Writing – review & editing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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References

[1] E.O. Hall, The deformation and ageing of mild steel: III discussion of results, Proc. Phys. Soc. B64 (1951) 747–753.

[2] N.J. Petch, The cleavage strength of polycrystals, J. Iron Steel Inst. 174 (1953) 25–28.

[3] E.O. Hall, Variation of hardness of metals with grain size, Nature 173 (1954) 948–949.

[4] R.Z. Valiev, Y. Estrin, Z. Horita, T.G. Langdon, M. Zehetbauer, Y.T. Zhu, Producing bulk ultrafine-grained materials by severe plastic deformation, J. Occup. Med. 58 (4) (2006) 33–42.

[5] Y. Iwahashi, Z. Horita, M. Nemoto M, T.G. Langdon, The process of grain refinement in equal-channel angular pressing, Acta Mater. 46 (1998) 3317–3331.

[6] R.Z. Valiev, Nanostructuring of metals by severe plastic deformation for advanced properties, Nat. Mater. 3 (2004) 511–516.

[7] R.Z. Valiev, T.G. Langdon, Principles of equal-channel angular pressing as a processing tool for grain refinement, Prog. Mater. Sci. 51 (2006) 881–981.

[8] A.P. Zhilyaev, T.G. Langdon, Using high-pressure torsion for metal processing: fundamentals and applications, Prog. Mater. Sci. 53 (2008) 893–979.

[9] T.G. Langdon, Twenty-five years of ultrafine-grained materials. Achieving exceptional properties through grain refinement, Acta Mater. 61 (2013) 7035–7059.

[10] R.B. Figueiredo, T.G. Langdon, Deformation mechanisms in ultrafine-grained metals with an emphasis on the Hall-Petch relationship and strain rate sensitivity, J. Mater. Res. Technol. 14 (2021) 137–159.

[11] F.A. Mohamed, Y. Xun, Correlations between the minimum grain size produced by milling and material parameters, Mater. Sci. Eng. A354 (2003) 133–139.

[12] J.R. Weertman, Hall-Petch strengthening in nanocrystalline metals, Mater. Sci. Eng. A166 (1993) 161–167.

[13] M. Furukawa, Z. Horita, M. Nemoto, R.Z. Valiev, T.G. Langdon, Microhardness measurements and the Hall-Petch relationship in an Al-Mg alloy with submicrometer grain size, Acta Metall. 44 (1996) 4619–4629.

[14] M.A. Meyers, A. Mishra, D.J. Benson, The deformation physics of nanocrystalline metals: experiments, Analysis, and Computations, J. Occup. Med. 58 (4) (2006) 41–48.

[15] T.G. Nieh, J. Wadsworth, Hall-Petch relation in nanocrystalline solids, Scripta Metall. Mater. 25 (1991) 955–958.

[16] N. Wang, Z. Wang, K.T. Aust, U. Erb, Room temperature creep behavior of nanocrystalline nickel produced by an electrodeposition technique, Mater. Sci. Eng. A237 (1997) 150–158.

[17] V. Yamakov, D. Wolf, S.R. Phillpot, A.K. Mukherjee, H. Gleiter, Deformation-mechanism map for nanocrystalline metals by molecular-dynamics simulation, Nat. Mater. 3 (2004) 43–47.

[18] I. Kovács, L. Zsoldos, Book "Dislocations and Plastic Deformation", Academy Press, Budapest, Hungary, 1973.

[19] H. Hasegawa, S. Komura, A. Utsunomiya, Z. Horita, M. Furukawa, M. Nemoto, T. G. Langdon, Thermal stability of ultrafine-grained aluminum in the presence of Mg and Zr additions, Mater. Sci. Eng. A265 (1999) 188–196.

[20] N. Tsuji, S. Okuna, T. Matsuura, Y. Koizumi, Y. Minamino, Mechanical properties as a function of grain size in ultrafine grained aluminum and iron fabricated by ARB and annealing process, Mater. Sci. Forum 426–432 (2003) 2667–2672.

[21] X. Chen, G. Huang, S. Liu, T. Han, B. Jiang, A. Tang, Y. Zhu, F. Pan, Grain refinement and mechanical properties of pure aluminum processed by accumulative extrusion bonding, Trans. Nonferrous Metals Soc. China 29 (2019) 437–447.

[22] R.W. Hayes, D. Witkin, F. Zhou, E.J. Lavernia, Deformation and activation volumes of cryomilled ultrafine-grained aluminum, Acta Mater. 52 (2004) 4259–4271.

[23] J. Gubicza, N.Q. Chinh, P. Szommer, A. Vinogradov, T.G. Langdon, Microstructural characteristics of pure gold processed by equal-channel angular pressing, Scripta Mater. 56 (2007) 947–950.

[24] T. Suzuki, A. Vinogradov, S. Hashimoto, Strength enhancement and deformation behavior of gold after equal-channel angular pressing, Mater. Trans. 45 (2004) 2200–2208.

[25] A. Vinogradov, T. Suyuki, S. Hashimoto, K. Kitagawa, A. Kuynetsov, S. Dobatkin, Structure and mechanical properties of submicrocrystalline copper produced by ECAP to very high strains, Mater. Sci. Forum 503–504 (2006) 971–976.

[26] B. Hadzima, M. Janecek, R.J. Hellmig, Y. Kutnyakova, Y. Estrin, Microstructure and corrosion behaviour of ultrafine-grained copper, Mater. Sci. Forum 503–504 (2006) 883–888.

[27] A.P. Zhilyaev, J. Gubicza, G. Nurislamova, Á. Révész, S. Surinnach, M.D. Baró, T. Ungár, Microstructural characterization of ultrafine-grained nickel, Phys. Status Solidi (2003) 263–271 (a) 198.

[28] K. Neishi, Z. Horita, T.G. Langdon, Grain refinement of pure nickel equal-channel angular pressing, Mater. Sci. Eng. A325 (2002) 54–58.

[29] T. Kolonits, Z. Czigány, L. Péter, I. Bakonyi, J. Gubicza, Influence of bath additives on the thermal stability of the nanostructure and hardness of Ni films processed by electrodeposition, Coatings 9 (2019) 644.

[30] N. Krasilnikov, W. Lojkowski, Z. Pakiela, R. Valiev, Tensile strength and ductility of ultra-fine-grained nickel processed by severe plastic deformation, Mater. Sci. Eng. A397 (2005) 330–337.

[31] N.Q. Chinh, Gy Horváth, Z. Horita, T.G. Langdon, A new constitutive relationship for the homogeneous deformation of metals over a wide range of strain, Acta Mater. 52 (2004) 3555–3563.