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Unified Hall-Petch description of nano-grain nickel hardness, flow stress and strain rate sensitivity measurements

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It is shown that: (i) nano-grain nickel flow stress and hardness data at ambient temperature follow a Hall-Petch (H-P) relation over a wide range of grain size; and (ii) accompanying flow stress and strain rate sensitivity measurements follow an analogous H-P relationship for the reciprocal "activation volume", (1/v*) = (1/A*b) where A* is activation area. Higher temperature flow stress measurements show a greater than expected reduction both in the H-P k_ε and in v*. The results are connected with smaller nano-grain size (< ~20 nm) measurements exhibiting grain size weakening behavior that extends to larger grain size when tested at very low imposed strain rates. [http://dx.doi.org/10.1063/1.4996294]

The yield stress, flow stress and hardness of conventional mm-scale grain size face-centered cubic and related metal structures are known to be raised by an order of magnitude at nano-scale grain size dimensions, ℓ, say, at $\ell \approx 20$ nm. At smaller grain size, the strength is reversed to decrease with further grain size reduction. Not so well known is that the strain rate dependence of the flow stress increases also by an order of magnitude during the same range of grain size strengthening. In the regime of grain size weakening, moreover, the strain rate dependence had been predicted on a grain size weakening constitutive equation basis to increase by a further order of magnitude. Our purpose here is to present a compilation of flow stress, hardness and strain rate sensitivity measurements for conventional and nano-grain nickel material, covering both grain size weakening and strengthening behaviors, and to provide an explanation of the measurements on the basis of a combined Hall-Petch inverse square root of ℓ dependence and thermal activation dislocation model description.

An early description of a Hall-Petch dependence for diamond pyramid hardness measurements obtained on electrodeposited polycrystalline nickel with microstructural coverage beginning from conventional sub-mm grain sizes and extending down to a smallest grain diameter of 12 nm had been given by Hughes et al.[1] The linear dependence had been drawn recently in Fig. 1 onto a compilation of conventional and ultrafine grain size nickel measurements[2] reported by Matsui et al.[3] in accordance with the relationship:

$$H = H_0 + k_H \ell^{-1/2} \tag{1}$$

The left-side listing of references is that given by Matsui et al. while the right-side listing applies for measurements added here and representing three rather diverse studies reported for nano-grain size nickel material: first, by Y.J. Li et al.[4] on stress-strain and strain rate "jumps" obtained in compression tests as a function of temperature; secondly, for comparable same type strain rate jumps obtained by Mohanty et al.[5] in miniature size specimen compression tests; and thirdly, by H. Li et al.[6] on strain rate sensitivity measurements made on mostly smaller nm grain size material tested in tension over an exceptionally wide range in strain rates and leading at smallest nm grain sizes to grain

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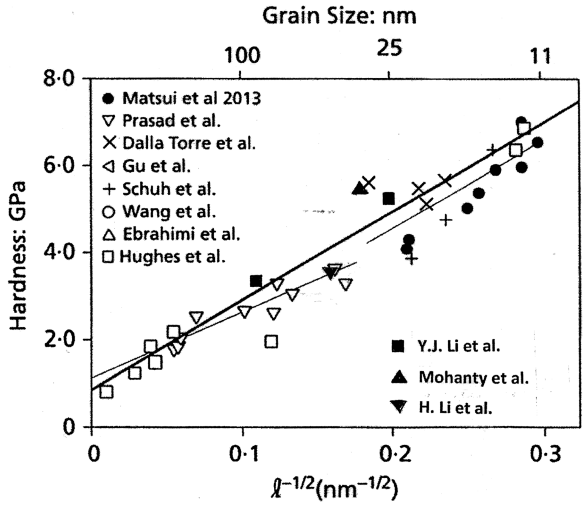

FIG. 1. Hall-Petch description of hardness dependence on grain size for nickel materials.

size weakening. In each case for the newer measurements, the initial 298 K flow stresses have been multiplied by 3 to calculate the hardness in the manner done by Hughes et al.[1]

The pair of filled square points in Fig. 1 came from representative true stress – strain curves reported by Y.J. Li et al.[4] at two nano-grain sizes. The material was produced by pulsed electrodeposition. The respective grain sizes were determined by x-ray diffraction. Strain rate "jumps" of 3 to 6 order-of-magnitude rate changes were conducted during the stress – strain tests. In general, larger stress jumps were observed at higher T; *a different result from conventional grain size measurements*. Minor or even negative strain hardening behavior was exhibited in the overall deformation curves. The filled-right-side-up triangle point in the figure for Mohanty et al.[5] had been obtained on micro-pillars of ~1.5 micron diameter fabricated with a focused ion beam technique. An average 30 nm grain size was determined in this case also by x-ray diffraction. Evidence of grain boundary sliding was reported from scanning electron microscope observations. The filled-downside-triangle point was obtained in tension by H. Li et al.[6] at a 40 nm grain size determined by transmission electron microscopy. This measurement was the only one credited to show "dislocation based deformation" when tested over higher strain rates of 10^{-4} to 2 s^{-1}. At smaller grain sizes extending down to 6 nm and at lower strain rates in the range of 10^{-10} to 10^{-6} s^{-1}, the reported stress – strain curves may be observed to show grain size weakening.

An explanation of the coupled grain size/strain rate/temperature dependencies of face-centered cubic (fcc) metals has been determined by combination of the dislocation pile-up model for the H-P relationship with a thermal activation description of dislocation motion. In Eq. 1, the H-P based flow stress, σ_ε, at strain, ε, relates to the hardness parameters through $\sigma_{0\varepsilon} = H_0/3$ and $k_\varepsilon = k_H/3$. And the dislocation pile-up model description of a concentrated stress, τ_C, in k_ε is given as[2,7]

$$k_\varepsilon = m_T[\pi m_S G b \tau_C/2\alpha]^{1/2}. \quad (2)$$

In Eq. (2), m_T and m_S are respectively Taylor and Sachs orientation factors, G is shear modulus, b is dislocation Burgers vector, and $\alpha \approx 0.8$ is an average factor for the dislocation character. For fcc copper, nickel and aluminum, the τ_C value in k_ε had been correlated with the cross-slip shear stress, τ_{III}, for example, as measured in single crystal tests.[2] Very importantly, the value of τ_C is assumed to be composed of $\tau_{CG} + \tau_{CTH}$ terms for athermal and thermal components of the shear stress in the grain boundary region.

For quantitative assessment of k_ε, we begin with the Hughes et al.[1] straight line H-P type hardness dependence in Fig. 1 at ambient temperature. A value of k_ε = 6.9 MPa.$mm^{1/2}$ is obtained when employing the multiplier of $(1/3)k_H$. Hughes et al. had assigned the k_ε value to an equivalent flow stress dependence at an effective strain, ε = 0.075. The value compares with k_ε = 7.3 MPa.$mm^{1/2}$ for the two points at 298 K of Y.J. Li et al.[4] in Fig. 1. Hughes et al. had obtained also an H-P

type model evaluation of k_ε = 5.3 MPa.mm$^{1/2}$ by employing independently reported single crystal cross-slip measurements. Very notably, as will be shown, the k_ε values for the Li et al.[4] flow stress measurements are determined to be reduced from the larger 7.3 MPa.mm$^{1/2}$ level to 4.84 MPa.mm$^{1/2}$ at 373 K. The estimated reduction in k_ε is larger than can be accounted for by a weaker temperature dependence of the single crystal cross-slip shear stress in Eq. (2) that was used by Hughes et al.[1] and so gives indication of an extent of grain boundary weakening having occurred at the higher temperature.

The strain rate jumps reported by Y.J. Li et al. provide an additional basis for investigation of the H-P behavior at nanoscale dimensions. Such connection had been established for copper and nickel materials on a thermal activation – strain rate (TASRA) basis by Armstrong and Rodriguez.[8] In this framework, the strain rate sensitivity is monitored by an activation volume parameter v* = A*b, in which A*, the activation area containing the dislocation Burgers vector, b, is given as

$$v^* = kT[\partial \ln(d\gamma/dt)/\partial\tau]_T. \quad (3)$$

In Eq. (3), k is Boltzmann's constant, T is temperature, $(d\gamma/dt)$ is shear strain rate, and τ is shear stress. The shear strain rate follows the relationship $(d\gamma/dt) = m_T(d\varepsilon/dt)$ for which m_T is the Taylor orientation factor of ~3.1. *On the basis of both $\sigma_{0\varepsilon}$ and k_ε being temperature and strain rate dependent, an H-P relationship for (1/v*) obtains*[8] *as*

$$(1/v^*) = (1/v^*)_0 + (k_\varepsilon/2m_T\tau_C v_C{}^*)\ell^{-1/2}. \quad (4)$$

In Eq. (4), the product $\tau_C v_C{}^* = \tau_{CG} v_C{}^* + \tau_{CTh} v_C{}^*$. At small strain, $\tau_C v_C{}^* \approx \tau_{CTh} v_C{}^* = W_0$, a constant, and this explains (1/v*) following an analogous H-P type equation.

Calculations of (b^3/v^*) derived from the measurements of Y.J. Li et al.,[4] Mohanty et al.[5] and H. Li et al.[6] are given in Table I. For H. Li et al., one might note that we used m_T in place of their $\sqrt{3}$ factor in determining v*. This measurement is particularly important because at the same grain size and at smaller values all tested at much lower strain rates, grain size weakening was measured. The tabulated v* values were computed for stress and strain rate changes done for the first jumps in the stress – strain curves except in the case of the two larger strain results for the 80 nm grain size material at 298 K in which case the v* values are for the first two jumps at ε = 0. 20 and ε = 0.27. The four ambient temperature measurements are added in Fig. 2 to the compilation of measurements previously reported by Armstrong and Rodriguez.[7] In general, v* is seen to be reduced in Table I at increasing ε for all of the measurements, as normally is associated with a reduced spacing of dislocation intersections, thus being contained in $(1/v^*)_0$, however, such effect is now shown in accordance with Eq. (4) to be contained in the H-P grain size term and so the same mechanism is taken to apply in the grain boundary regions. Furthermore, the result shown in Table I of *v* decreasing at the lower stresses measured at higher temperatures is not usual* and this requires explanation because of the otherwise well-established[9] reciprocal dependence of v* on τ_{Th}.

The v* calculations were obtained on the assumption of $\partial\tau$ in Eq. (3) being equal to the change in thermal stress component, $\Delta\tau_{Th}$, and this may not be true for the current measurements

TABLE I. Activation "volume", v* = A*b, values determined from strain-rate-sensitivity (SRS) measurements made on nanopolycrystalline nickel materials.

Reference	ℓ, nm	T, K	σ, GPa	ε	v*, 10^{-19} mm^3	b^3/v^*
Y.J. Li et al.[4]	25	298	1.72	0.10	3.67	0.0425
	25	373	1.53	0.10	3.06	0.051
	80	298	1.11	0.20	14.7	0.0106
	80	298	1.105	0.27	4.55	0.0343
	80	373	1.02	0.13	9.17	0.017
	80	418	0.93	0.10	8.26	0.019
	80	473	0.92	0.08	7.75	0.020
Mohanty et al.[5]	30	298	1.80	~0.025	4.77	0.033
	30	335.5	1.73	~0.025	4.30	0.036
	30	373	1.60	~0.025	3.82	0.040
H. Li et al.[6]	40	300	1.175	0.01	5.4	0.031

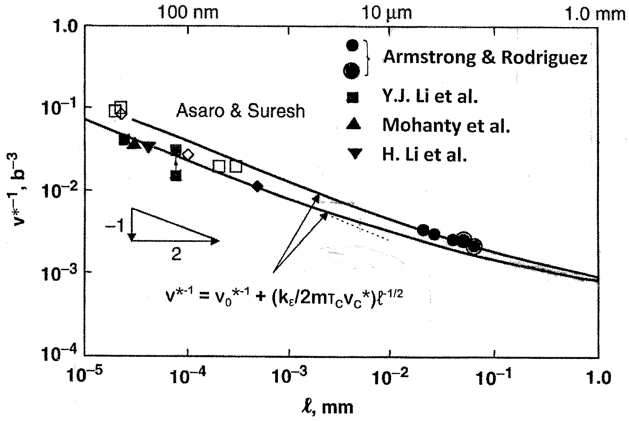

FIG. 2. Hall-Petch type dependence of reciprocal "activation volume", (1/v*), calculations for nickel (and copper); the upper and lower H-P curves are for 77 and 300 K respectively.

at higher temperatures. The incremental shear stress, $\Delta\tau$, could possibly contain an athermal stress component, $\Delta\tau_G$. Such is certainly true for the τ_C value in Eq. (4) as had been described.[8] On this basis, the problem with the v* measurement would be that there was also an increase in dislocation density which occurred during a strain rate jump. Thus, the measured (1/v*) obtained from Eq. (3) would include an additional component from a change in dislocation density, $\Delta\rho$, producing $\Delta\tau_G$ as

$$(1/v^*) = (1/v^*)_{Th} + (1/kT)(\Delta\tau_G/\Delta\ln[d\varepsilon/dt])_T. \quad (5)$$

In this manner, a relative increase in $\Delta\tau_G$ accompanying the change in $\Delta\tau_{Th}$, in the grain boundary region gives one possible explanation for the anomalous reduction in v* with decrease in σ_ε at the higher temperatures listed in Table I. Such concern for the v* dependence can be traced to the original description of dislocation velocity in the Orowan equation leading to v* being a function essentially only of τ_{Th}; for example, see Armstrong.[9]

Alternatively, significantly smaller values of v* are associated with the decrease in stress accompanying grain boundary weakening behavior. Such observation applies for the tensile stress measurements of H. Li et al.[6] at very small grain sizes and very low strain rates. The concern relates to the negative strain hardening for the Y.J. Li et al.[4] measurements as well as to the grain boundary sliding observations of Mohanty et al.[5] The consideration of such grain size weakening at smaller ℓ values is often expressed in the generalized constitutive equation[10]

$$(d\varepsilon/dt) = (AD_L Gb/kT)(b/\ell)^p(\sigma/G)^q. \quad (6)$$

Equation (6) was proposed to model deformation controlled by grain boundary sliding. In the equation, D_L is an appropriate boundary diffusion coefficient, T is temperature, and A, p and q are experimental constants. Typically, p and q take on values of 1.0 or 2.0. From Eq. (6)

$$(1/v^*) = \sigma/m_T kTq. \quad (7)$$

Rodriguez and Armstrong had employed Eq. (7), with q = 1.0, to compute for nano-zinc (1/v*) values significantly higher than a highest value of $(1/b^3)$ for a+c slip in the grain boundary regions.[11] Similarly higher (1/v*) values were obtained for nano-twinned copper that was shown to follow an H-P flow stress dependence.[9] The same type of result is now seen to be In agreement with the grain size weakening measurements reported by H. Li et al. The reported (b^3/v^*) values, in accordance with Eq. (3), are 0.83, 0.5, 0.9 and 0.2 for respective grain sizes of 6, 20, 30 and 40 nm grain sizes when tested at the very low, creep-type, strain rates mentioned earlier. The values compare with Eq. (7) calculations of 0.65-1.40, 0.65-1.64, 0.98-1.40, and 0.52-1.44 for respective stresses of 500-1000, 500-1250, 750-1000 and 400-1100 MPa. The higher values of (b^3/v^*) are seen to approach a further order of magnitude greater than the highest grain size strengthening values listed in Table I and shown in Fig. 2, including the one Li et al. value reported for grain size strengthening at a much higher strain rate.

Other measurements reported by Rajaraman et al.[12] on H-P type grain size strengthening for pulse-deposited nickel material of 17 nm provide a useful example for less favorable comparison with those measurements shown in Figs. 1 and 2. Comparable H-P values of $\sigma_{0\varepsilon}$ = 426 MPa and k_ε = 5.5 MPa.mm$^{1/2}$ were reported at ambient temperature for the initial yield behavior that was followed by negative strain hardening thereafter over a broad range of strain rates. A flow stress of 2.05 GPa and multiplier of 3 for hardness value at a lowest strain rate of 0.04 s^{-1} produces reasonable agreement with the H-P line in Fig. 1 despite separate measurement being reported of lower nanoindentation hardness values in the range of ~4.8-5.1 GPa. A reported logarithmic strain rate sensitivity of 0.0064 at the 2.05 GPa flow stress gives a low value of $(b^3/v^*) = 0.017$ for comparison with the Fig. 2 results.

In summary, the assembled flow stress, hardness and strain rate sensitivity measurements demonstrate via their related Hall-Petch dependencies a unifying assessment of nano-grain nickel material deformation behavior covering the regimes of grain size strengthening and weakening. Quite reasonable agreement has been obtained, first, for a Hall-Petch description of strength properties obtained from three rather diverse investigations. Secondly, the (1/v*) characterization of strain rate sensitivity measurements has been connected in a reasonably quantitative manner to the dislocation pile-up model description for the H-P term involving k_ε and which thermal activation parameter is shown to provide a sensitive marker for eventual transition to the onset of weakening at smaller nano-grain sizes, especially, in tests at lower creep-related strain rates.

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