

“Finer Grains Are Stronger” Fails, and Not Because the Theoretical Strength Was Reached

— the prediction at **10 nm**, **1550 MPa**, is only **14.09** per cent of the theoretical **11000 MPa** — the formula reaches theoretical strength at a grain size of **0.187652 nm**, smaller than the **0.256 nm** atomic spacing — what acts is the grain-boundary volume fraction, **30** per cent at **10 nm** — [Paper 397]

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— *From thinking to syncing.* —

Abstract

The Hall–Petch relation says finer grains are stronger, and it reverses at 10 to 30 nm. This paper shows that the reversal is not because the theoretical strength was reached—the prediction there does not even reach 14 per cent of it. No new theorem or law is claimed. First, $\sigma = \sigma_0 + k/\sqrt{d}$ diverges as $d \rightarrow 0$; the formula has no ceiling of its own (Section 1). Second, the prediction at $d = 10$ nm is **1550 MPa** (Section 2). Third, and this is the core of the paper. That is only **14.09** per cent of the theoretical strength $E/10 = 11000$ MPa (Section 2). Fourth, the formula reaches theoretical strength at **0.187652 nm**, smaller than copper’s 0.256 nm atomic spacing (Section 3). Fifth, at 10 nm the grain boundary occupies **30** per cent of the volume; at 100 nm it is **3** per cent (Section 3). Sixth, the separator is whether deformation is carried by dislocations or by grain-boundary sliding (Section 5).

Scope of this paper (scope note): No new theorem or law is claimed—the Hall–Petch relation, its inverse regime, grain-boundary sliding and estimates of theoretical strength are all known in materials science. No material is designed—alloy composition and processing are not given. Only the numbers inside one formula are examined. No mechanism for the reversal is claimed—which of grain-boundary sliding, grain rotation or dislocation-source starvation dominates is disputed, and this paper does not decide it. Only that it is not the theoretical strength. The constants are not claimed as measurements— $\sigma_0 = 50$ MPa and $k = 0.15$ MPa·m^{1/2} are representative values with copper in mind. No definition of theoretical strength is built— $E/10$ is a classical estimate; a more careful value depends on crystal and plane. Ductility is not treated—only strength; the loss of ductility with grain refinement is not the subject. Relation to earlier papers: Paper 386 showed that the rate moves with the solubility fixed—here a different quantity begins to act while the strength formula stays put. Paper 389 showed that length, not thickness, is what binds—here it is the volume fraction, not the theoretical strength. Paper 385 showed that the grip term makes the maximum—here the boundary term makes the failure. Paper 300 showed that same-root and different-root can be decided—dislocation strengthening and boundary softening are different-root by that criterion. What is added is putting numbers on strength and volume fraction at six grain sizes, showing that 10 nm reaches only 14.09 per cent of theoretical strength, showing that the formula reaches it only below the atomic spacing, obtaining 39 atoms across a 10 nm grain, and placing the separator at “dislocations or boundary sliding”.

1. Notation and the Question

Setting: write the Hall–Petch relation.

$$\sigma = \sigma_0 + \frac{k}{\sqrt{d}}, \quad \sigma_0 = 50 \text{ MPa}, \quad k = 0.15 \text{ MPa} \cdot \text{m}^{1/2}$$

Take the boundary thickness as $\delta = 1$ nm and estimate the volume fraction as $3\delta/d$. With copper in mind, $E = 110$ GPa and the theoretical strength is $E/10$.

Observation 1.1

the formula diverges as $d \rightarrow 0$. Through $1/\sqrt{d}$ —it has no ceiling of its own.

Observation 1.2

experiment, however, reverses at 10 to 30 nm. Beyond that, finer is weaker—there is a place where the formula fails.

Observation 1.3

the plausible explanation is “it reached the theoretical strength”.Hitting a ceiling——this paper checks that with numbers.

Question: why does the Hall–Petch relation fail?

2. Even at 10 nm It Is 14.09 Per Cent of Theoretical Strength

Computation 2.1: predicted strength and boundary volume fraction against grain size (computed in this paper).

Grain size d	Predicted strength [MPa]	Boundary volume fraction	Fraction of theoretical
100 μm	65.0000	0.00003	0.0059
10 μm	97.4342	0.0003	0.0089
1 μm	200.0000	0.0030	0.0182
100 nm	524.3416	0.0300	0.0477
20 nm	1110.6602	0.1500	0.1010
10 nm	1550.0000	0.3000	0.1409

Observation 2.2

this is the core of the paper.At the 10 nm where the reversal is observed, the last column is still 0.1409——14.09 per cent of theoretical strength: it fails with more than a factor of seven left in hand.

Observation 2.3

even at the coarse end of the reversal band it is under 11 per cent.0.1010 at 20 nm——nowhere in the band is theoretical strength close.

Observation 2.4

the boundary volume fraction, by contrast, reaches 0.3000 at 10 nm. Three tenths of the material is boundary—at 100 nm it is still 0.0300, an order of magnitude less.

Observation 2.5

the two quantities grow at different rates. Strength as $1/\sqrt{d}$, volume fraction as $1/d$ —the finer the grain, the faster the fraction takes over.

Observation 2.6

a 10 nm grain is 39 atoms across. Copper’s atomic spacing is 0.256 nm—a size at which treating it as a continuum becomes doubtful.

3. The Formula Reaches Theoretical Strength Only Below One Atom

Computation 3.1: grain size at which the formula gives $E/10 = 11000$ MPa (computed in this paper).

$$d = \left(\frac{k}{E/10 - \sigma_0} \right)^2 = 1.876525 \times 10^{-10} \text{ m} = 0.187652 \text{ nm}$$

Quantity	Value
Grain size at theoretical strength	0.187652 nm
Atomic spacing in copper	0.256 nm
Ratio	0.7330 (smaller than an atom)

Observation 3.2

the formula reaches theoretical strength only for grains smaller than a single atom. 0.187652 nm against 0.256 nm—which is to say, physically unreachable.

Observation 3.3

so “it saturates at the theoretical strength” does not hold. The grain becomes smaller than an atom before the ceiling arrives——there is no opportunity to hit it.

Observation 3.4

the plausible explanation was off by orders of magnitude. The observed reversal is at 10 to 30 nm——between 53 and 160 times the 0.19 nm at which the formula reaches theoretical strength.

Observation 3.5

the shape is that of Paper 389. There length rather than thickness was what bound——here the volume fraction rather than the theoretical strength. In both, the quantity that gets named is not the one that acts.

Observation 3.6

the volume fraction does not appear in the formula at all. Only σ_0 and $k/\sqrt{d}$ ——a quantity that is absent from the formula beginning to act: that is what the failure is.

4. What Fails Is Not the Formula but Its Premise

Observation 4.1

Hall--Petch presumes dislocation pile-up. Boundaries stop dislocations and the pile-up concentrates stress——the smaller the grain, the fewer dislocations it can hold.

Observation 4.2

a 10 nm grain holds only a few. Thirty-nine atoms across——and the picture of a pile-up stops making sense.

Observation 4.3

the boundary itself starts carrying the deformation instead. Sliding and rotation of grain boundaries——when three tenths of the volume is boundary, that becomes the leading process.

Observation 4.4

so the formula did not fail; its premise disappeared. The formula remains correct——one has simply left the region where it applies.

Observation 4.5

they are different-root by the criterion of Paper 300. Dislocation strengthening is set inside the crystal, boundary softening at the interface——two things with different roots stand behind one word, “strength”.

5. Separator: Dislocations, or Boundary Sliding

Observation 5.1

separator——does deformation happen inside the crystal or at the interfaces.

Grain size	Carrier of deformation	Boundary volume fraction	Refining gives
> 100 nm	dislocations	3 per cent or less	more strength
< 10 nm	boundary sliding	30 per cent or more	less strength

Observation 5.2

the last column points opposite ways. The same operation gives the opposite result——which region one is in reverses the remedy.

Observation 5.3

the boundary is set by the volume fraction. Three per cent against thirty—not by any absolute value of the strength.

Observation 5.4

the separator can be moved. In a material with a thinner boundary δ , the reversal should occur at a finer grain size—a testable prediction.

Observation 5.5

to be honest—both $\sigma_0 = 50$ MPa and $k = 0.15$ are representative values with copper in mind. They differ by material—what does not move is that the grain size at theoretical strength is smaller than the atomic spacing, and that the volume fraction grows as $1/d$.

Observation 5.6

one last thing—“it stopped because it hit the ceiling” is most suspect precisely when the ceiling is in view. Put in the numbers and there was still a factor of seven to go—what stopped it was a quantity that is not in the formula.

6. Roll Call and Closing

1. $\sigma = \sigma_0 + k/\sqrt{d}$ diverges as $d \rightarrow 0$ (Section 1): **no ceiling of its own.**
2. 1550 MPa at 10 nm (Computation 2.1): **the prediction.**
3. 14.09 per cent of theoretical (Computation 2.1): **a factor of seven in hand.**
4. 10.10 per cent even at 20 nm (Computation 2.1): **nowhere close.**
5. 30 per cent boundary at 10 nm (Computation 2.1): **3 per cent at 100 nm.**
6. Strength $1/\sqrt{d}$, fraction $1/d$ (Observation 2.5): **different growth.**
7. A 10 nm grain is 39 atoms across (Observation 2.6): **continuum doubtful.**
8. Theoretical strength at 0.187652 nm (Computation 3.1): **smaller than an atom.**

9. **53 to 160 times from the observed reversal (Observation 3.4): orders of magnitude off.**

10. **The volume fraction is not in the formula (Observation 3.6): an absent quantity acts.**

Closing: the Hall–Petch relation says finer grains are stronger, and it reverses at 10 to 30 nm—but that reversal is not because the theoretical strength was reached. The formula $\sigma = \sigma_0 + k/\sqrt{d}$ diverges as $d \rightarrow 0$ and has no ceiling of its own—so the plausible explanation is that it hit the theoretical strength. This paper checks that with numbers. The prediction at 10 nm, **1550 MPa**, is only **14.09** per cent of the theoretical $E/10 = 11000$ MPa—it fails with more than a factor of seven left in hand. Even at 20 nm it is 10.10 per cent, so nowhere in the reversal band is theoretical strength close. The boundary volume fraction, meanwhile, reaches **0.3000** at 10 nm against 0.0300 at 100 nm. Strength grows as $1/\sqrt{d}$ and the fraction as $1/d$, so the finer the grain the faster the fraction takes over. And the formula reaches theoretical strength only below the size of one atom— $d = (k/(E/10 - \sigma_0))^2 = \mathbf{0.187652}$ nm, smaller than copper’s 0.256 nm atomic spacing, which is to say physically unreachable. “It saturates at the theoretical strength” therefore does not hold: the grain becomes smaller than an atom before the ceiling arrives. The observed reversal at 10 to 30 nm is between 53 and 160 times that size, so the plausible explanation was off by orders of magnitude. As in Paper 389, the quantity that gets named is not the one that acts. What fails is not the formula but its premise—Hall–Petch presumes dislocation pile-up, and a 10 nm grain, thirty-nine atoms across, holds only a few dislocations, so the picture of a pile-up stops making sense. The boundary itself starts carrying the deformation when three tenths of the volume is boundary. The formula remains correct; one has simply left the region where it applies. By the criterion of Paper 300 they are different-root: dislocation strengthening inside the crystal, boundary softening at the interface. And the volume fraction does not appear in the formula at all—a quantity absent from the formula beginning to act is what the failure is. One thing does the separating—does deformation happen inside the crystal or at the interfaces. Above 100 nm dislocations lead and refining strengthens; below 10 nm boundary sliding leads and refining weakens. The boundary between the two regions is set by the volume fraction, three per cent against thirty, not by any absolute value of the strength. In a material with a thinner boundary the reversal should occur at a finer grain size, which is a testable prediction. To be honest—both $\sigma_0 = 50$ MPa and $k = 0.15$ are representative values with copper in mind and differ by material. What does not move is that the grain size at theoretical strength is smaller than the atomic spacing, and that the volume fraction grows as $1/d$. One last thing—“it stopped because it hit the ceiling” is most suspect precisely when the ceiling is in view. Put in the numbers and there was still a factor of seven to go. What stopped it was a quantity that is not in the formula.

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