Hall–Petch Breakdown at Elevated Temperatures

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The Hall–Petch effect responsible for the strength of fine-grained and ultrafine-grained (UFG) metals is almost exclusively measured at room temperature. One reason for this is that at elevated temperatures grains tend to coarsen, and this negates the strengthening. The grains may, however, be stabilized by small volume fractions of fine dispersoids. These dispersoids cause *direct* Orowan strengthening and, by stabilizing the so-called Zener grain size, *indirect* strengthening due to Hall–Petch. We show that for most metals the critical Zener grain size *above* which Hall–Petch strengthening is more important than Orowan strengthening is lower than, and sometimes even considerably lower than 1 μm , i.e., in the range of UFG metals. Breakdown of the Hall–Petch relationship, which occurs at elevated temperatures once mechanisms weaker than Hall–Petch start to control the strength, is best studied for grain sizes well above this critical grain size. The Hall–Petch breakdown due to either Coble creep or grain size-dependent dislocation creep is modeled. We present model calculations for copper and verify our approach by comparing with experimental results for ferritic steels containing nanoscale dispersoids. [doi:10.2320/matertrans.MA201309]

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1. Introduction

A common feature of Hall–Petch measurements^{1,2)} to study the strengthening of materials due to grain refinement is that they are almost always carried out at room temperature, regardless of the melting point of the material. However, depending on the absolute melting point T_m of a material, its homologous temperature T/T_m at room temperature may vary considerably—for example, it is 0.1 for molybdenum and 0.43 for zinc. Materials with low homologous temperatures (e.g., $T/T_m < 0.2$) will deform athermally at room temperature. The room temperature deformation of materials with higher homologous temperatures, on the other hand, will involve thermally activated processes characterized by an Arrhenius-type temperature dependence of the strength. Sometimes, in order to be able to study these processes at room temperature, alloys exhibiting high homologous temperatures and diffusivities at room temperature are chosen such as in the work of Kim *et al.*³⁾ for Mg–Li alloys.

At sufficiently high homologous temperatures the observed strength will drop below that expected for the Hall–Petch relationship. In other words, the Hall–Petch relationship breaks down, or, briefly, Hall–Petch breaks down. This does not necessarily mean that the Hall–Petch mechanism, whatever it is, ceases to exist at elevated temperatures, but that some other, weaker deformation mechanism begins to control the strength. As a result of the Hall–Petch breakdown, the typical fine-grain strengthening may turn into softening; the “strengthening” contribution becomes negative. Some explanations for the so-called inverse Hall–Petch effect in which the room temperature strength decreases with decreasing grain size are based on thermally activated processes such as Coble creep, grain boundary sliding, or recovery of dislocations at grain boundaries that become more important as the grain size decreases and more diffusion paths become available.^{4–7)} Put differently, by sufficiently reducing the grain size of a material, thermally activated deformation processes may be probed at room temperature.

Instead of increasing the homologous temperature at room temperature by reducing the melting point, or instead of refining the grains, a more direct way to probe thermally activated processes is to raise the test temperature. Such tests are rarely carried out for materials with “normal” grain sizes such as 10 μm and above. Ultrafine-grained (UFG) materials with grain sizes as small as ~ 20 nm, on the other hand, are sometimes tested above room temperature.⁷⁾ This is not a trivial task since small grains like to coarsen at homologous temperatures as low as $T/T_m = 0.3$,⁸⁾ and large grains do not result in significant Hall–Petch strengthening. Therefore, tests to assess the Hall–Petch breakdown at elevated temperatures are best carried out with fine-grained materials exhibiting a stable grain size.

Methods to stabilize small grain sizes at elevated homologous temperatures do exist. An elegant approach is to reduce the grain boundary free energy to zero by segregating the correct amount of an appropriate element at the grain boundaries. Then the driving force for grain boundary migration becomes zero and the grains ought to be stable.⁹⁾ An additional advantage of this approach is that the segregating element does not cause any additional strengthening as long as its solubility in the matrix is sufficiently low. Atomistic simulations by Millet *et al.*¹⁰⁾ support this concept, but only a few systems such as Y–Fe,⁹⁾ and Ni–W, Ni–B and Ni–S¹⁰⁾ have so far shown experimental promise. Also, it appears that direct experimental evidence for zero free grain boundary energies, i.e., the absence of grooving at grain boundaries intersecting a free surface, does not exist. An additional complication is found in the work of Gorkaya *et al.*¹¹⁾ who have shown that grain boundary migration may be driven not only by the grain boundary free energy, but also by an externally applied shear stress. Therefore, even when the grain boundary free energy is zero, grain coarsening may occur during mechanical testing.

Instead of reducing the grain boundary free energy to zero, grain coarsening may also be inhibited by pinning the grain boundaries with small particles. For any population of stable particles with a given size and number density, grain

Table 1 Values published for the proportionality factor C_Z in the Zener equation $d_Z = C_Z d_p / f$.

C_Z	Remarks	Reference
$4/3 = 1.334$	Analytical calculation	Quoted in Manohar <i>et al.</i> ²²⁾
$1/6 = 0.1667$	Analytical calculation; C_Z in agreement with wide range of experimental data	Rios ²¹⁾
0.074	Finite element simulation; C_Z lower than for Manohar experimental results	Fig. 12 in Coutourier <i>et al.</i> ²³⁾
0.70	Monte Carlo simulation; C_Z higher than for Manohar experimental results	
0.2	Compilation of experimental results	Manohar <i>et al.</i> ²²⁾
0.12	Phase field model calculation	Shahandeh <i>et al.</i> , ²⁴⁾ using 0.667 for the value of σ in their Zener equation

coarsening will stop once a limiting “Zener grain size” has been reached.¹²⁾ The pinning particles may be precipitates produced by heat treatments or dispersoids introduced by methods such as internal oxidation or mechanical alloying. Dispersoids such as Y_2O_3 are preferred over precipitates because they tend to be extremely resistant to coarsening or dissolution. There are many examples for such oxide dispersion-strengthened (ODS) materials.^{13–15)} Because of the high stability of many ceramic particles in metallic systems, Zener pinning may be applied almost universally to stabilize grain sizes.

The problem with dispersoids in fine-grained materials is that they may obscure the Hall–Petch strengthening by introducing an additional strengthening mechanism, namely, Orowan strengthening. Hazzledine, in his two-page 1992 paper,¹⁶⁾ has discussed this problem. First, he calculated the Orowan strengthening for a given population of dispersoids, i.e., the *direct* strengthening. Second, he calculated the Zener grain size, i.e., the grain size at which the grain boundaries are fully anchored by the dispersoids. Third, he calculated the Hall–Petch strengthening, i.e., the *indirect* strengthening arising from the fine grains stabilized by the dispersoids. Using representative values for the Hall–Petch coefficient Hazzledine showed that the Hall–Petch strengthening exceeds the Orowan strengthening for dispersoid sizes > 0.8 nm. Since experimentally observed dispersoids are typically much larger than 0.8 nm Hazzledine concluded that Hall–Petch strengthening is expected to always dominate Orowan strengthening. While this is true for many materials, a survey of a number of metallic systems will show the need to qualify this statement.

The purpose of the present work is two-fold. First, based on Hazzledine’s model, the critical particle size d_p^* or the critical Zener grain size d_Z^* above which Hall–Petch strengthening exceeds Orowan strengthening will be calculated for a range of pure metals at room temperature. It will be seen that the critical sizes are very much material-dependent. For grain sizes well above d_Z^* the strength is primarily determined by Hall–Petch strengthening, and Hall–Petch breakdown experiments are best performed for such grain sizes. The second purpose of this work is an analysis of the mechanisms responsible for Hall–Petch breakdown at elevated temperatures. Coble creep¹⁷⁾ as well as a model for grain size-dependent dislocation creep recently proposed by Blum and Zeng^{18,19)} will be used to estimate the temperatures above which mechanisms weaker than predicted by the classic Hall–Petch relationship govern the strength. The Hall–Petch breakdown will be illustrated for pure copper and

verified by comparing with experimental results for ferritic stainless steels containing nanoscale dispersions.

2. The Hazzledine Model for Indirect vs. Direct Strengthening

The Hazzledine model for the ratio between Hall–Petch (*indirect*) and Orowan (*direct*) strengthening requires an expression for the Zener grain size. The Zener grain size d_Z is, roughly speaking, that grain size at which the driving force $2\gamma/r$ due to the curvature of grain boundaries having a specific grain boundary free energy γ is balanced by the pinning action of the particles. For a given particle dispersion, it is the smallest grain size that is thermally stable. Experimentally, the Zener grain size d_Z may be stable at temperatures up to homologous temperatures of $T/T_m \sim 0.7$.²⁰⁾ It is proportional to the dispersoid diameter d_p according to:

$$d_Z = C_Z \times \frac{d_p}{f}, \quad (1)$$

where C_Z is a constant and f the volume fraction of the dispersoids. A commonly used value for C_Z is $4/3$. However, as shown by Rios²¹⁾ and Manohar *et al.*,²²⁾ experimentally observed values for the Zener grain size are several times smaller than those calculated with $C_Z = 4/3$. As an additional complication, the experimental and the calculated values for the Zener grain size are subject to considerable variation (Table 1). For example, Coutourier *et al.*²³⁾ show that different types of simulations actually bracket the experimental results compiled by Manohar.²²⁾ Since the C_Z values from the analysis of Rios²¹⁾ and the experimental compilation by Manohar *et al.*²²⁾ in Table 1 agree quite well with each other, the Zener equation, for the purpose of this paper, is written as:

$$d_Z = \frac{d_p}{6f}. \quad (2)$$

Following Hazzledine,¹⁶⁾ the yield stress σ_y for a pure metal at low homologous temperature is:

$$\sigma_y = \sigma_0 + \sigma_{OR} + \sigma_{HP}. \quad (3)$$

Hereby σ_0 is the matrix yield stress or “friction stress” for an infinite grain size (or some orientation-averaged value of the single-crystal yield stress), σ_{OR} is the Orowan strengthening due to the dispersoids and σ_{HP} the Hall–Petch strengthening due to the grains. The Orowan contribution may be written as:¹⁶⁾

Fig. 1 Illustration of the dependencies of the Orowan and Hall-Petch stress on the Zener grain size, with $M = 3.06$, $f = 0.01$ and values representative for copper, i.e., $G = 42.2$ GPa, $b = 0.256$ nm and $k_{\text{HP}} = 0.14$ MPa m^{1/2}. The critical Zener grain size d_z^* is that size for which Hall-Petch and Orowan strengthening are equal.

$$\sigma_{\text{OR}} = M \left(\frac{6f}{\pi} \right)^{1/2} \frac{Gb}{d_p}, \quad (4)$$

where M is the Taylor factor, G the shear modulus and b the Burgers vector. With the help of eq. (2), the Orowan contribution may also be written as a function of the Zener grain size:

$$\sigma_{\text{OR}} = M \left(\frac{1}{6\pi f} \right)^{1/2} \frac{Gb}{d_z}. \quad (5)$$

The Hall-Petch strengthening corresponding to the Zener grain size is:

$$\sigma_{\text{HP}} = k_{\text{HP}} \times d_z^{-1/2}. \quad (6)$$

Figure 1 illustrates how the Orowan and Hall-Petch stresses depend on the Zener grain size (which in turn is controlled by the dispersoid size and volume fraction). Above a critical Zener grain size d_z^* (to be calculated further down) the Hall-Petch stress becomes larger than the Orowan stress. This might suggest that experiments to study the Hall-Petch breakdown are best carried out for large dispersoids where Hall-Petch dominates. Larger dispersoids result however in larger Zener grain sizes and consequently a pronounced decrease of the Hall-Petch effect. Therefore one would expect a certain window for the Zener grain size which is particularly suited for experimental observations.

With eq. (2) for the Zener grain size we obtain for the ratio of the Hall-Petch and the Orowan strengthening either:

$$\frac{\sigma_{\text{HP}}}{\sigma_{\text{OR}}} = \frac{\pi^{1/2} k_{\text{HP}}}{M G b} d_p^{1/2} \quad (7)$$

or

$$\frac{\sigma_{\text{HP}}}{\sigma_{\text{OR}}} = \frac{(6\pi f)^{1/2} k_{\text{HP}}}{M G b} d_z^{1/2}. \quad (8)$$

The critical particle size d_p^* and critical Zener grain size d_z^* above which Hall-Petch strengthening exceeds Orowan strengthening are obtained by setting $\sigma_{\text{HP}}/\sigma_{\text{OR}}$ in eqs. (7) and (8) equal to 1 and solving for d_p^* or d_z^* , respectively:

$$d_p^* = \frac{M^2}{\pi} \left[\frac{G b}{k_{\text{HP}}} \right]^2 \quad (9)$$

and

$$d_z^* = \frac{M^2}{6\pi f} \left[\frac{G b}{k_{\text{HP}}} \right]^2. \quad (10)$$

Equations (9) and (10) show that the critical sizes depends strongly on the ratio of the shear modulus and the Hall-Petch coefficient k_{HP} . The critical dispersoid size is independent of the dispersoid size and the dispersoid volume fraction, while the critical Zener grain size is independent of the dispersoid size, but depends on the dispersoid volume fraction.

3. Critical Dispersoid Sizes and Critical Zener Grain Sizes — Experimental Assessment

Table 2 summarizes materials parameters for a range of fcc, bcc and hcp metals. From these parameters the critical dispersoid size and critical Zener grain size above which Hall-Petch strengthening exceeds Orowan strengthening are calculated. It should be pointed out that these sizes are subject to considerable uncertainty, since the Hall-Petch coefficients of many metals are not precisely known. For example, Hall-Petch coefficients for ferritic iron compiled in Table 3 vary from 0.1 to 1.6 MPa m^{1/2}. There are several reasons for these variations. First, the Hall-Petch coefficient may depend on the grain size. It may *increase* with decreasing grain size as seen by a comparison between the Hall-Petch coefficients compiled by Wu *et al.*³³⁾ for ultra-fine/nanocrystalline metals with those in Table 2. But it may also *decrease* with decreasing grain size as in the inverse Hall-Petch effect.^{4-6,34)} Second, the Hall-Petch coefficient of steels may increase strongly with increasing carbon concentration—the value of ~ 0.1 MPa m^{1/2} for an interstitial-free steel increases to ~ 0.55 MPa m^{1/2} when 60 ppm carbon are added.³¹⁾ Third, in most measurements of the Hall-Petch coefficient it is implicitly assumed that a random polycrystalline texture or grain size-independent texture is established which may not necessarily hold true. Fourth, in order to determine a “true” Hall-Petch coefficient one should subtract all other strengthening contributions such as precipitation or dispersion strengthening.³⁵⁾ The data for the Hall-Petch coefficients in Table 2 were chosen to be “reasonable”, but for the time being we can only hope that the substantial variations for the different metals in that Table are not primarily due to microstructural differences, but that they are actually meaningful. Obviously, when experimenting with a particular metal in a particular microstructural state, its Hall-Petch coefficient needs to be verified.

Ignoring these complications, Table 2 shows that the calculated critical dispersoid sizes and critical Zener grain sizes vary substantially from metal to metal. With the exception of niobium (~ 300 nm and ~ 5 μm), they tend to be smaller for bcc and hcp metals as compared to fcc metals. This is because the Hall-Petch coefficients in bcc materials tend to be higher than those in fcc and hcp materials.³³⁾ Some of the critical dispersoid sizes are extremely small, such as 1.3 nm for molybdenum or 0.5 nm for zinc. Such sizes are difficult to produce experimentally—the smallest particles observed to date appear to be the ~ 2 nm nanoclusters seen in 14YWT steels.³⁶⁾ Also, if the particle size becomes too small, Zener pinning may not be effective at elevated temperatures

Table 2 Materials constants for selected fcc, bcc and hcp metals. Assuming a dispersoid volume fraction of $f = 0.01$ (1%), the critical dispersoid sizes and critical Zener grain sizes above which Hall–Petch strengthening dominates Orowan strengthening are listed in the last two rows of the table.

Sources:

Melting points, Burgers vectors, shear moduli: Frost and Ashby²⁵⁾

Hall–Petch coefficients for Al, Ag, Cr, Nb, Mo, W, Zn (at 0°C), Mg, α -Ti: Armstrong²⁶⁾

Hall–Petch coefficient for Cu: Hansen²⁷⁾

Hall–Petch coefficient for Ni: Thompson²⁸⁾

Hall–Petch coefficient for α -Fe: Takaki *et al.*²⁹⁾

Hall–Petch coefficient for Ta: Jankowski *et al.*³⁰⁾

	Al	Ag	Cu	Ni	α -Fe	Cr	Nb	Mo	Ta	W	Zn	Mg	α -Ti
Melting point T_m , °C	660	962	1085	1455	1538	1907	2477	2623	3017	3422	420	650	1668
Melting point T_m , K	933	1235	1358	1728	1811	2180	2750	2896	3290	3695	693	923	1941
Homologous temperature T/T_m at 300 K	0.322	0.243	0.221	0.174	0.166	0.138	0.109	0.104	0.091	0.081	0.433	0.325	0.155
Burgers vector b , nm	0.286	0.286	0.256	0.249	0.248	0.25	0.286	0.273	0.286	0.274	0.267	0.321	0.295
Shear modulus $G(300\text{ K})$, GPa	25.4	26.4	42.1	78.9	64	126	44.3	134	61.2	160	49.3	16.6	43.6
Friction stress σ_0 , MPa	15.7	37.3	20	21.8	100	179	68.7	108	152	641	32.4	6.9	78.5
Hall–Petch coefficient k_{HP} , MPa m ^{1/2}	0.068	0.068	0.14	0.158	0.6	0.9	0.04	1.77	0.556	0.788	1.02	0.279	0.403
Critical particle size d_p^* , nm	34.0	36.7	17.7	46.1	2.1	3.7	299	1.3	3.0	9.2	0.5	1.1	3.0
Critical Zener grain size d_Z^* , nm ($f = 0.01$)	567	612	294	768	35	61	4983	21	49	154	8	18	51

Table 3 Compilation of Hall–Petch coefficients published for ferritic steels.

Description of steel	Hall–Petch coefficient, MPa m ^{1/2}	Reference
Interstitial-free ferritic iron	0.1	Takeda <i>et al.</i> ³¹⁾
Decarburized iron (proportional limit)	0.2	Embury ³²⁾
Ferritic steel with 60 ppm carbon	0.55	Takeda <i>et al.</i> ³¹⁾
Commercial iron powder	0.6	Takaki <i>et al.</i> ²⁹⁾
Mild steel	0.74	Armstrong ²⁶⁾
Ultrafine/nanocrystalline Fe	1.6	Wu <i>et al.</i> ³³⁾

because thermal activation may assist the unpinning of grain boundaries. In contrast to molybdenum and zinc, the critical sizes for aluminum, i.e., a dispersoid size of 34 nm and a Zener grain size of 0.6 μm , are within easy reach of experiments. Therefore, Hazzledine's¹⁶⁾ statement that in experimentally attainable situations the indirect strengthening always exceeds the direct strengthening is not universally true.

4. Models for the Hall–Petch Breakdown at Elevated Temperatures

Equation (6) for the Hall–Petch strengthening is temperature-independent. Following Hirth and Lothe³⁷⁾ and assuming that Poisson's ratio is temperature-independent, the Hall–Petch equation may be written as:

$$\sigma_{HP}(T) = \left[\frac{G(T)}{G(300\text{ K})} \right]^{1/2} k_{HP}(300\text{ K}) \times d^{-1/2}, \quad (11)$$

i.e., the temperature dependence of the Hall–Petch strength is controlled by the temperature dependence of the shear modulus G . As a result, Hall–Petch strengthening shows a mild decrease with increasing temperature. The Orowan stress in eqs. (4) and (5) is proportional to the temperature-dependent shear modulus, and the same is assumed to hold true for the friction stress σ_0 .

As the temperature is increased, the measured yield stress drops eventually below the predicted Hall–Petch strength, i.e., Hall–Petch breaks down. A large variety of thermally activated mechanisms may be responsible for this. According to Mukherjee³⁸⁾ the steady-state strain rate for these creep mechanisms may in general be written as:

$$\dot{\epsilon} = A \frac{D_0 G b}{k T} \times \left(\frac{b}{d} \right)^p \times \left(\frac{\sigma}{G} \right)^n \times \exp \left(- \frac{Q}{RT} \right), \quad (12)$$

where A is a materials parameter, D_0 and Q the preexponential factor and activation energy for the appropriate value of the self-diffusivity (either in the bulk or in the grain boundaries), p a constant, n the stress exponent and R the molar gas constant. Solving eq. (12) for σ one obtains:

$$\sigma = \left(\frac{k T G^{n-1} \dot{\epsilon}}{A D_0 b} \right)^{1/n} \times \left(\frac{d}{p} \right)^q \times \exp \left(\frac{Q}{n R T} \right), \quad (13)$$

where $q = p/n$ is the grain size exponent. The grain size exponent may take on values such as $q = -1/2$,^{18,19)} $q = 0$ (conventional dislocation creep, see Poirier¹⁷⁾), $q = 1$ (Padmanabhan *et al.*,⁶⁾ as long as their threshold stress is set to 0), $q = 2$ (Ma *et al.*,³⁹⁾ as long as their threshold stress is set to zero); Nabarro–Herring creep¹⁷⁾ and $q = 3$ (Coble creep¹⁷⁾). With the exception of Nabarro–Herring and Coble creep, the absolute values of the creep stresses given by these models are subject to considerable uncertainty because not all relevant parameters are well known. Experimentally, discrimination between the different models is therefore best made on the basis of the temperature, grain size and strain rate dependence of the measured stress.

The Coble creep and the Blum–Zeng model bracket the range of the proposed grain size exponents and are derived on the basis of clear physical assumptions. For a given strain rate $\dot{\epsilon}$ and temperature T , the Coble creep stress is:¹⁷⁾

$$\sigma_C = \frac{k T d^3 \dot{\epsilon}}{47 \Omega \delta_B D_{B0}} \exp \left(\frac{Q_B}{RT} \right) \quad (14)$$

where k is Boltzmann's constant, Ω the atomic volume, δ_B the grain boundary width and D_{B0} and Q_B the pre-exponential

Fig. 2 Illustration of the Hall-Petch breakdown due to Coble creep in copper according to eqs. (11) and (14) using the parameters listed in Tables 2 and 4. The grain size is indicated next to each curve. For the 0.5 μm grain size, the full range of the Hall-Petch and Coble creep relationships is depicted (see broken lines).

Fig. 3 Illustration of the Hall-Petch breakdown due to Blum-Zeng creep in copper according to eqs. (11) and (15) using the parameters listed in Tables 2 and 4. The grain size is indicated next to each curve.

Table 4 Parameters used for the simulations for copper in Figs. 2 and 3.

Physical quantity	Value	Reference
Atomic volume Ω , m^3	1.18×10^{-29}	Frost and Ashby ²⁵⁾
Temperature coefficient of shear modulus $\frac{T_m}{G(300\text{K})} \frac{dG}{dT}$	-0.54	"
Product of grain boundary width and pre-exponential factor for grain boundary diffusion $\delta_B D_{B0}$, m^3/s	5×10^{-15}	"
Activation energy for grain boundary diffusion Q_B , kJ/mole	104	"
Taylor factor	3.06	Blum and Zeng ¹⁸⁾
Poisson's ratio ν	0.34	Smithells <i>et al.</i> ⁴⁰⁾
Parameter α in eq. (15)	0.3	Blum and Zeng ¹⁸⁾
Parameter c in eq. (15)	0.7	Blum and Zeng ¹⁹⁾

factor and activation energy for the grain boundary self diffusion coefficient $D_B = D_{B0} \exp(-\frac{Q_B}{RT})$.

In the Blum-Zeng model^{18,19)} the Hall-Petch breakdown is due to grain size-dependent steady-state dislocation creep. Using eq. (1) in Blum and Zeng's 2011 publication¹⁹⁾ with simplifying assumptions made there, the strength may be written as:

$$\sigma_{BZ} = G \left[\frac{\pi(1-\nu)M^3}{1.24} \right]^{1/8} \times \alpha \left[\frac{1-c+c^3}{c^3} \right]^{1/2} \times \left[\frac{kT\dot{\epsilon}}{GbD_{B0}} \right]^{1/8} \times \exp\left(\frac{Q_B}{8RT}\right) \times \left(\frac{d}{b}\right)^{-1/2} \quad (15)$$

where ν is Poisson's ratio, M the Taylor factor, α a dislocation interaction constant [eq. (15) in Blum and Zeng¹⁸⁾] and c a parameter that stands for four constants f_j , f_{rel} , f_b and f_{dip} the values of which are assumed to be equal to c in Blum and Zeng.¹⁹⁾ Furthermore, $\delta_B = b$ is assumed in eq. (15). For the sake of completeness it is pointed out that eq. (18) in Blum and Zeng's 2009 publication¹⁸⁾ reduces to eq. (15) above if it is solved for σ , the resulting expression is multiplied with a factor of $\frac{\delta_B}{b} (1-\nu)^{1/8}$ and the value of ξ in their function $f(\xi)$ is taken to be zero, resulting in $f(\xi) = 1$.

The strengths given by the Coble creep and the Blum-Zeng models have not only different grain size exponents, i.e., $q = 3$ vs. $q = -1/2$, but their strain rate sensitivities are also quite different, namely, 1 and 1/8. Testing at different strain rates may therefore be used to discriminate between the

two models. Also, the temperature dependence of the stresses for the two mechanisms is different, namely, approximately $\exp(\frac{Q_B}{RT})$ and $\exp(\frac{Q_B}{8RT})$, i.e., the Blum-Zeng creep stress drops off more slowly with increasing temperature than the Coble creep stress.

5. Modeling of the Hall-Petch Breakdown for Copper

Figures 2 and 3 illustrate the Hall-Petch breakdown at elevated temperatures in pure copper due to Coble or Blum-Zeng creep [eqs. (14) and (15)] assuming that grain coarsening does not occur. The parameters for the simulations are taken from Tables 2 and 4. The figures show that, for the grain sizes considered, Hall-Petch breakdown due to Blum-Zeng creep occurs at lower temperatures than for Coble creep, i.e., Blum-Zeng creep is expected to control the temperature at which the breakdown occurs. Because of its lower activation energy, $Q_B/8$, the Blum-Zeng creep strength drops off more slowly with increasing temperature than the Coble creep strength. Not surprisingly, the temperature at which the Hall-Petch breakdown due to Coble creep sets in increases strongly with increasing grain size. For the Blum-Zeng mechanism, on the other hand, the breakdown temperature is almost independent of the grain size. In fact, if the friction and Orowan stresses are zero or negligible, the breakdown temperature is grain size independent, since the strengths given by the Hall-Petch and Blum-Zeng mechanisms exhibit exactly the same grain size dependence.

Table 5 Experimentally determined yield stresses and calculated strengthening contributions for several oxide dispersion-strengthened ferritic stainless steels at 300 K (for experimental data see Schneibel *et al.*²⁰⁾).

Material	Nominal composition of matrix, mass%	Grain size d , μm	Measured yield stress σ_y , MPa	Volume fraction f of Dispersoids	Dispersoid size, nm	Friction stress σ_0 , MPa	Calculated Orowan stress σ_{OR} , MPa	Calculated Hall–Petch stress σ_{HP} , MPa	Calculated yield stress σ_{calc} , MPa	$\frac{\sigma_{HP}}{\sigma_{OR}}$, calculated	Adjusted yield stress, σ_y^{adj} , MPa
Kanthal-A1	Fe–20Cr–5.5Al–0.5Ti	546	410	0	—	400	0	26	426	0.00	300
PM2000	"	25	698	0.008	16.2	400	371	120	891	3.09	627
PM2000	"	1.1	830	0.008	16.2	400	371	572	1343	0.65	945
14YWT	Fe–14Cr–3W–0.4Ti	0.5	1469	0.00031	1.8	400	657	849	1905	0.77	1340
14YWT	"	0.2	2050	0.00217	2.4	400	1303	1342	3044	0.97	2142

Fig. 4 Measured yield stresses vs. temperature for ferritic stainless steels²⁰⁾ (solid lines) and comparison with the Hall–Petch and Blum–Zeng models (broken lines).

Fig. 5 Comparison between calculated and measured yield stresses for ferritic stainless steels (see Table 5). The slope and regression coefficient of the line fitted to the data are indicated.

Measuring the grain size dependence of the breakdown temperature may help to identify the strength-controlling mechanisms. Similarly, since the strengths given by Coble and Blum–Zeng depend in different ways on the strain rate, measurements of the strain rate dependence of the strength would also be useful.

6. Modeling of the Hall–Petch Breakdown for Ferritic Stainless Steels and Comparison with Experimental Data

There is a dearth of experimental data for the temperature dependence of the yield stress in fine-grained materials with stable grain sizes. Arguably, the best compilation of data is found in Schneibel *et al.*²⁰⁾ for the nanocluster-strengthened steel 14YWT and the ODS steel PM2000. These data are shown in Fig. 4 together with data for the dispersion-free version of PM2000, namely, Kanthal-A1.²⁰⁾ In order to access as wide a range of grain sizes as possible we assume that the differences in the chemical compositions of the three types of steel are negligible as far as their mechanical properties are concerned. Table 5 is a compilation of the relevant microstructural parameters. It contains also the measured room temperature yield stresses, a reasonable value for the friction stress σ_0 obtained from the Kanthal-A1 data in Fig. 4, the Orowan stresses calculated from eq. (4), the Hall–Petch stresses calculated from eq. (11) and the

calculated ratio of the Hall–Petch (*indirect*) to the Orowan (*direct*) strengthening. Figure 5 indicates a reasonably linear relationship between the measured and calculated yield stresses. However, the calculated yield stresses are on average a factor of 1.42 larger than those measured. Assuming this factor to be due to inaccuracies in the strengthening models and microstructural parameters, the three strengthening contributions and thus the total value of the calculated yield stress were scaled down by a factor 1/1.42 in order to better match the experimental data (see last column of Table 5). The parameters used for modeling the Hall–Petch breakdown due to the Blum–Zeng model are listed in Tables 2 and 6. The value of the parameter c was chosen such as to give reasonable agreement with the drop-off in the yield stress at elevated temperatures. The fitted curves are shown by the broken lines in Fig. 4. For the grain sizes 0.2, 0.5 and 1.1 μm reasonable agreement is obtained for the yield stress below $\sim 500^\circ\text{C}$ given by $\sigma_y = \sigma_0 + \sigma_{OR} + \sigma_{HP}$ and the Blum–Zeng model above $\sim 500^\circ\text{C}$. The fits to the experimental curves involved essentially two adjustable parameters, one to match the strength at low temperatures (the factor 1/1.42), and one to match the strength for temperatures above the Hall–Petch breakdown, i.e., the value of $c = 0.15$. In order to keep Fig. 4 simple, the model calculations for 25 and 546 μm are not shown. For these grain sizes the calculated curves fall below the experimental data (because of the relatively

Table 6 Parameters used for the simulations for ferritic steel in Fig. 4.

Physical quantity	Value	Reference
Atomic volume Ω , m ³	1.18×10^{-29}	Frost and Ashby ²⁵⁾
Temperature coefficient of shear modulus $\frac{T_m}{G(300K)} \frac{dG}{dT}$	-0.81	"
Scaling factor to adjust the calculated friction stress, Orowan stress and Hall–Petch coefficient at 300 K in Table 5 (see Fig. 5)	1/1.4212	
Adjusted friction stress σ_0^{adj} at 300 K, MPa	281.45	
Adjusted Hall–Petch coefficient, $k_{\text{HP}}^{\text{adj}}$ at 300 K, MPa m ^{1/2}	0.423	
Product of grain boundary width and pre-exponential factor for grain boundary diffusion $\delta_B D_{B0}$, m ³ /s	1.1×10^{-12}	"
Activation energy for grain boundary diffusion Q_B , kJ/mole	174	"
Taylor factor	3.06	Blum and Zeng ¹⁸⁾
Poisson's ratio ν	0.29	Smithells <i>et al.</i> ⁴⁰⁾
Parameter α in eq. (13)	0.3	Blum and Zeng ¹⁸⁾
Parameter c in eq. (13)	0.15	Fitted to data in Fig. 5

low friction stress σ_0^{adj} , see Table 5) and, in addition, the calculated Hall–Petch breakdown temperatures are quite low: 290°C for 25 μm and 205°C for 546 μm . The match might be improved by adding a temperature-dependent friction stress to the Blum–Zeng model, but it is questionable that this would result in a more conclusive interpretation. All that can be said at the present time is that the Blum–Zeng model is reasonably consistent with the Hall–Petch breakdown. In future experiments it would be preferable to choose pure metals with negligibly low friction stresses and with grain sizes well above the critical Zener grain sizes in Table 2. The direct Orowan strengthening would then be relatively unimportant and the strength for temperatures below the temperature at which the Hall–Petch breakdown sets in would be almost exclusively determined by the Hall–Petch mechanism. This would facilitate identification of the mechanism which causes Hall–Petch breakdown at elevated temperatures. As a result, an unambiguous and conclusive comparison between models and experiments for the Hall–Petch breakdown may be possible.

7. Summary and Conclusions

(1) Traditionally, Hall–Petch strengthening is almost always measured at room temperature. Depending on the material, room temperature corresponds to homologous temperatures ranging from ~ 0.1 to ~ 0.4 , i.e., thermally activated processes may or may not occur in traditional Hall–Petch measurement.

(2) Dispersion-strengthened metals exhibit an extremely stable grain size, the Zener grain size. The Zener grain size above which Hall–Petch (*indirect*) strengthening dominates Orowan (*direct*) strengthening varies from 8 nm for zinc to $\sim 5 \mu\text{m}$ for niobium. Materials with grain sizes well above these critical sizes lend themselves to measuring the Hall–Petch breakdown at elevated temperatures.

(3) The breakdown of the Hall–Petch relationship at elevated temperatures is due to control by other mechanisms the strength of which depends in different ways on temperature, grain size and strain rate. Coble creep and Blum–Zeng grain size-dependent dislocation creep bracket the range of proposed grain size dependencies.

(4) The Hall–Petch breakdown due to Coble creep and Blum–Zeng creep has been modeled for copper. The Hall–Petch breakdown due to Blum–Zeng creep has been modeled for oxide dispersion-strengthened ferritic steels and seen to be in reasonable agreement with experimental measurements for PM2000 and 14YWT steels, thus lending support to the Blum–Zeng model.

(5) Measurements of the yield stress vs. temperature for oxide dispersion-strengthened pure metals with different grain sizes and for different strain rates would be desirable for a more conclusive identification of the mechanism(s) for Hall–Petch breakdown at elevated temperatures.

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