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YIELD STRESS OF NANOCRYSTALLINE MATERIALS

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Abstract. Modeling of strengthening by nanocrystalline materials need consideration of both dislocation interactions and sliding due to Coble creep acting simultaneously. Such a mechanism is considered in this paper. It is shown that a model based on using Coble creep (with a threshold stress) for finer grains and conventional Hall-Petch strengthening for larger grains, appears to be most successful in explaining experimental results provided a grain size distribution is incorporated into the analysis to account for a distribution of grain sizes occurring in most specimens. Use of an alternate formalism of Coble creep proposed recently gives a somewhat less satisfactory agreement with experiments.

1. INTRODUCTION

The classic Hall-Petch relationship [1,2] describes the relationship between yield stress τ and grain size *d*, *viz.,*

$$\tau = \tau_0 + kd^{-1/2}, \tag{1}$$

where τ_0 is the friction stress considered needed to move individual dislocations, and *k* is a constant (often referred to as the Hall-Petch slope and is material dependent). This equation is well behaved for grains larger that about a micron.

Masumura *et al.* [3] have plotted some of the available data in a Hall-Petch plot. It is seen that the yield stress-grain size exponent for relatively large grains appears to be very close to -0.5 and generally this trend continues until the very fine grain regime (~100 nm) is reached. With the advent of nanocrystalline materials whose grain sizes are of nanometer (nm) dimensions, the applicability and validity of Eq. (1) becomes of interest in view of recently compiled experimental results [4].

A close analysis of experimental Hall-Petch data in a variety of materials shows that although the plot of τ *vs.* $d^{-1/2}$ forms a continuous curve, three different regions can be seen *viz.*: (1) a region from single crystal to a grain size of about a micron (μ) where the classical Hall-Petch description can be used; (2) a region for grain sizes ranging from about a μ to about 30 nm where the Hall-Petch relation roughly holds, but deviates from the classical -0.5 exponent to a value near zero and (3) a region beyond a very small critical grain size where the Hall-Petch slope is nearly zero with no increase in strength on decreasing grain size or where the strength actually decreases with decreasing grain size. Although some of the measurements on which the trend discussed above is based on are not entirely reliable because of a variety of reasons discussed recently by Sanders *et al.* [5], the above delineation into three regions is beginning to be accepted. In this paper we are mostly interested in the mechanism applicable to the third (lowest grain sizes) region. However it is possible to obtain expression for yield stress applicable to any grain size.

2. DISLOCATION MODELS

For large grain sizes (region I) there are a number of models which have been proposed to account for the grain size dependence of the stress, τ, in Eq. (1); most of which can be rationalized in terms of a dislocation pile up model. These are reviewed in detail by Li and Chou [6]. In deriving the Hall-Petch relation, the role of grain boundaries as a barrier to dislocation model is considered in various models. In

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one type of model [7,8,9], the grain boundary acts as a barrier to pile up of dislocations, causing stresses to concentrate and activating dislocation sources in the neighboring grains, thus initiating slip from grain to grain. In the other type of models [10,11] the grain boundaries are regarded as dislocations barriers limiting the mean free path of the dislocations, thereby increasing strain hardening, resulting in a Hall-Petch type relation. A review of the various competing theories of strengthening by grain refinement has been discussed by several workers. (For a survey, see Lasalmonie and Strudel [12].) It is clear that a variety of processes, both dislocation and non-dislocation based, could be postulated. It is possible that several of these processes could compete or reinforce the deformation process.

Pande and Masumura [13] by considering the conventional Hall-Petch model showed that a dislocation theory for the Hall-Petch effect only gives a linear dependence of τ on $d^{-1/2}$ when there are large number of dislocations in a pile-up and plasticity is not source limited. For the intermediate region one can assume that the conventional models are still applicable with some modifications due to relatively smaller grain sizes. The model of Pande and Masumura [13] assumes that the classical Hall-Petch dislocation pile up model is still dominant with the sole exception that the analysis must take into account that in the nanometer size grains where the number of dislocations within a grain cannot be very large. Further at still smaller grain sizes, this mechanism should cease when there are only two dislocations in the pile-up. In this regime, the yield stress increases as d decreases because the pile-ups contain few dislocations, the stress concentration a the head falls and a larger applied stress is required to compensate. When the number of dislocations falls to one, no further increase in the yield stress is possible and it saturates.

If the number of dislocations n in a pile up is not too large the length of the pile up L is not linear in n but an additional term is necessary. Chou[14] gives the relation

$$L \cong \frac{A}{2\tau}\left[4(n+m-1) - 2i_1\left(\frac{2n}{3}\right)^{1/3}\right], \qquad (2)$$

where $i_1 / (6)^{1/3} = 1.85575$. Pande and Masumura [13] using a result from Szego [15] give an improved expression *viz.,*

$$L = \frac{A}{2\tau}\left[2(n+m-1)^{1/2} - \frac{i_1+\varepsilon}{(12)^{1/3}(n+m-1)^{1/6}}\right]^2, \qquad (3)$$

where ε is a small correction term ($\varepsilon << 1$) and can be neglected. They find that for small grain sizes there are additional terms to Hall-Petch relation *viz.*,

$$s = l^{-1/2} + c_1(l^{-1/2})^{5/3} + c_2(l^{-1/2})^{7/3}, \qquad (4)$$

where $l = Lm\tau / 2A$, $s = \tau/[m\tau^*]$, $c_1 = -0.68811$ and $c_2 = 0.21339$.

This model recovers classical Hall-Petch at large grain sizes but for smaller grain sizes the τ levels off. This model therefore cannot explain a drop in τ for very fine grained materials. One can of course assume that dislocation sources must operate in each grain, and so an additional component of the yield stress exists of at least *GB/d* and therefore yield stress should rise as d^{-1}. However as shown by Yamakov *et al.* [16] such a possibility is not likely.

There are other dislocation model such as due to Valiev *et al.* [17], Malygin [18] and Gryaznov *et al.* [19]. The latter proposed a generalization of the of Hall-Petch relationship to describe the slope in all three regions discussed above. Their approach is to assume the polycrystal as a composite material whose components are a crystalline matrix with layers (assumed to be oblate ellipsoids) of interfaces. By making judicious assumptions and approximations, they were able to develop a formulation that can account for all three response regions and determine the critical value where the Hall-Petch slope becomes zero.

3. MECHANISM INVOLVING COBLE CREEP

As mentioned earlier our main interest here is the consider the third region. Clearly, at sufficiently small grain sizes, the Hall-Petch model based upon dislocations may not be operative. However in this region it is believed that a new mechanism of deformation may be operative called Coble creep or grain boundary diffusional creep. It is a deformation process that leads to homogeneous elongation of grains along the tensile direction. It is usually believed that the strain rate is given as :

$$\varepsilon = \frac{c\tau\Omega\delta D_{gb}}{k_B T d^3}, \qquad (5)$$

where δ is the width of the diffusing channel (approximately equal to the grain boundary width), D_{gb} is the diffusion constant for a grain boundary, T is the temperature, k_B is Boltzmann's constant, τ is the applied stress, Ω is the activation volume (usually of the order of atomic volume = $a^3/4$ for an FCC lattice) and c is a proportionality constant that depends upon the grain shape. From Eq. (5), $\tau = Bd^3$ where

$$B = \frac{\varepsilon k_B T}{c\Omega\delta D_{gb}}. \qquad (6)$$

Chokshi *et al*. [20] have proposed room temperature Coble creep as the mechanism to explain their results. Certainly, there is an order of magnitude agreement and the trend is correct, however, the functional dependence of τ on d is incorrect as pointed out by Neih and Wadsworth [21]. Conventional Coble creep demands as shown above that $\tau \sim d^3 \propto (d^{-1/2})^{-6}$, *i.e.,* the τ vs. $d^{-1/2}$ curve falls very steeply as $d^{-1/2}$ increases. This is not found experimentally [20].

Chokshi *et al.* [20] showed that their data fits better a relation of the form

$$\tau = \beta - K' d^{-1/2}, \qquad (7)$$

where β and K' are constants. Eq. (7) cannot be related simply to any known mechanism but a plausible explanation for this experimental fact was suggested by Masumura *et al*. [3]. In their model it is assumed that that polycrystals with a relatively large average grain size obey the classical Hall-Petch relation (the departure from the linear Hall-Petch relation in pile up model discussed above is ignored (Eq. (4) in the first approximation but can be incorporated easily). For very small grain sizes, it is assumed that Coble creep is active. The statistical nature of the grain sizes in a polycrystal is taken into consideration by using an analysis similar to Kurzydlowski [22]. The volume of the grains are assumed to be log-normally distributed,

$$f(\nu) = \frac{1}{\nu\sqrt{2\pi(s_{ln\nu})^2}} \times \exp\left[\frac{-(\ln\nu - m_{ln\nu})^2}{2(s_{ln\nu})^2}\right], \qquad (8)$$

where $m_{ln\nu}$ and $s_{ln\nu}$ are the mean value and standard deviation of $\ln\nu$, respectively and where the m_ν is the mean volume of all the grains,

$$m_\nu = \int_0^\infty \nu f(\nu)d\nu = \exp\left[m_{ln\nu} + \frac{(s_{ln\nu})^2}{2}\right] \qquad (9)$$

and can also be written as $m_\nu = k(\bar{d})^3$ where $\bar{d}$ is mean grain size and with being a geometrical shape factor equal to 1.4 for this analysis. Finally, it is assumed that a grain size d^* exists at which value of grain size the classical Hall-Petch mechanism switches to the Coble creep mechanism, *i.e.,* $\tau_{hp} = \tau_c$ at $d = d^*$. This model gives an analytical expression for τ as a function of the inverse square root of d in a simple and approximate manner that could be compared with experimental data over a whole range of grain sizes. A major consideration in this approach is what explicit expression to use for Coble creep. Eq. (6) was not found to be suitable since it led to an extremely steep drop of τ with $d^{-1/2}$. This paper attempts to answer this question by considering two different expressions for Coble creep and using them to obtain expressions for a Hall-Petch type relation valid for all grain sizes.

In the model of Masumura et al. [3] the τ vs. d relationship used for Coble creep is given by

$$\tau_c = A/d + Bd^3, \qquad (10)$$

where B is both temperature and strain-rate dependent as given in (6) but has an additional term. This threshold term A/d can be large if d is in the nanometer range. For intermediate grain sizes, both mechanisms might be active if the specimen has range of grain size distribution. Others (Sastry [23]) have also proposed a threshold of the form A/d.

In a recent publication Yamakov et al. [16] have tried to extend Eq. (6) to smaller grain sizes. The relation they obtained is

$$\varepsilon = \frac{4G\tau\Omega D_{gb}}{k_B T}\left[\frac{2\delta}{d^3} - \frac{\delta^2}{d^4}\right] \qquad (11)$$

and assuming that δ/d<<1, this can be rewritten as

$$\tau = A' d^2 + B' D^3,$$

$$A' = \frac{k_B T}{16G\Omega D_{gb}}$$

and $\qquad (12)$

$$B' = \frac{k_B T}{8\delta G\Omega D_{gb}},$$

where G is a constant and where the other terms are defined as in Eq. (5).

Now using the formalism of Masumura *et al.* [3] and using the above two expressions for Coble creep by turn we obtain the corresponding expressions of yield stress and compare them. Using Eqs.(1) and (10), we have

$$k(d^*)^{-1/2} = \frac{A}{d^*} + B(d^*)^3 \tag{13}$$

from which d^* can be determined. Then the yield stress after averaging is given as

$$\langle \tau - \tau_0 \rangle = F_{hp} + F_c, \tag{14}$$

where

$$F_{hp} = \frac{1}{m_\nu} \int_{\nu^*}^{\infty} \tau_{hp} \nu f(\nu) d\nu \tag{15}$$

and

$$F_{hp} = \frac{1}{m_\nu} \int_{\infty}^{\nu^*} \tau_{hp} \nu f(\nu) d\nu, \tag{16}$$

Defining

$$\xi = \frac{\bar{d}}{d^*}, \quad \sigma = s_{ln\nu} \tag{17}$$

and

$$\Lambda(\xi,\sigma,\alpha) = \xi^{3\alpha} \exp\left[\frac{\sigma^2}{2}\alpha(\alpha+1)\right] \tag{18}$$

and

$$\Phi(\xi;\sigma,\alpha) = \mathrm{erf}\left[\left(\frac{1}{2\sigma^2}\right)\left(\ln\left\{\frac{\nu}{m_\nu}\right\} - \frac{\sigma^2}{2}\alpha(\alpha+1)\right)\right], \tag{19}$$

where erf is the error function. Now we can write

$$F_{c1} = \frac{A}{2d^*} f_{c1}, \quad f_{c1} = \Lambda\left(\xi;\sigma,-\frac{1}{3}\right)\left[\Phi\left(\xi;\sigma,-\frac{1}{3}\right)+1\right] \tag{20}$$

and

$$F_{c2} = B\frac{(d^*)^3}{2} f_{c2}, \quad f_{c2} = \Lambda(\xi;\sigma,1)\left[\Phi(\xi;\sigma,1)+1\right]. \tag{21}$$

Using Eq. (14), we have a normalized form of the yield stress as a function of the scaled grain size ξ, grain size parameter σ, and p,

$$\frac{2}{k(d^*)^{-1/2}} \langle \tau - \tau_0 \rangle = f_{hp} + \frac{p f_{c1} + f_{c2}}{1+p}, \tag{22}$$

where

$$p = \frac{A/d^*}{B(d^*)^3}. \tag{23}$$

The term p is the ratio of Coble threshold stress to conventional stress evaluated at d^* where the transition from Coble creep to Hall-Petch strengthening occurs. For each p and σ, a universal curve is obtained with the form and shape of the curve similar to experimental data.

The corresponding expression of Yamakov *et al.* [16] for Coble creep, Eq. (12), can also be developed by the formalism given above. The Hall-Petch contribution and the volume creep dependence are same. The only modifications required are the replacement of the threshold term, Eq. (20) to one that involving the grain boundary diffusion,

$$F'_{c1} = A'\frac{(d^*)^2}{2} f'_{c1}, \quad f'_{c1} = \Lambda\left(\xi;\sigma,-\frac{1}{3}\right)\left[\Phi\left(\xi;\sigma,-\frac{1}{3}\right)+1\right], \tag{24}$$

the replacement of B by B' in Eq. (21) and defining

$$p' = \frac{A'(d^*)^2}{B'(d^*)^3}. \tag{25}$$

This leads to

$$\frac{2}{k(d^*)^{-1/2}} \langle \tau - \tau_0 \rangle = f_{hp} + \frac{p' f'_{c1} + f'_{c1}}{1+p'} \tag{26}$$

in a completely analogous development to Eq. (23).

4. RESULTS AND DISCUSSIONS

Fig. 1 gives the expression of the normalized yield stress as a function of (normalized grain size) raised to -1/2 and the Coble creep to influenced by a threshold term given in Eq. (10). For three different values of σ, which represents the width of the grain size distribution (large σ indicates wider distribution). The values of s are the ones typically seen in the experimental distribution of grain sizes. Here p

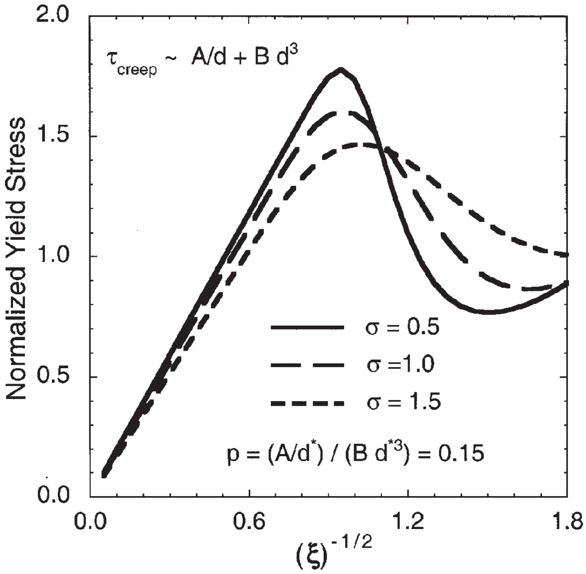

Fig. 1. Normalized yield stress as function of $\xi^{-1/2}$ for the Coble creep with a threshold stress for three different values of σ where *p* is held constant.

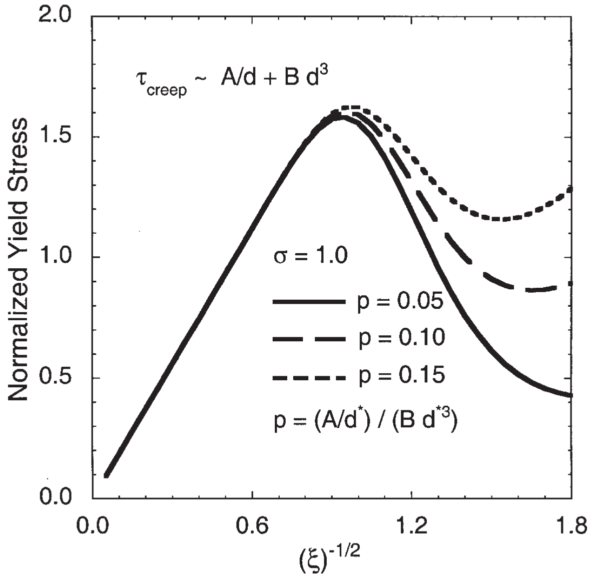

Fig. 2. Normalized yield stress as function of $\xi^{-1/2}$ for the Coble creep with a threshold stress for three different values of *p* where ξ is held constant.

is a constant given by Eq. (22). As seen the theoretical curves represent well the form of the curve seen experimentally. Fig. 2 is a similar plot where the effect of various values of *p*, Eq. (22), is shown. So far there is no independent way of obtaining the values of *p* to be utilized in the calculations. Notice that at higher *p* the decrease in yield stress at lower grain sizes is very much reduced.

Figs. 3 and 4 show the results of a similar calculation but using a different Coble creep expression where grain boundary diffusion is considered. Fig. 3 shows the effect of various σ whereas Fig. 4 shows the effect of various *p′* values. For a given σ, the effect of *p′* is minimal. The shape of the curve appears to be qualitatively similar to those in Figs. 1 and 2. Therefore only very precise experimental

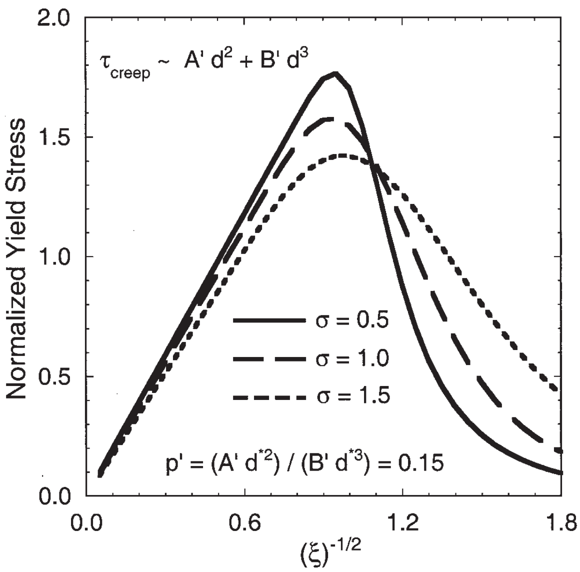

Fig. 3. Normalized yield stress as function of $\xi^{-1/2}$ for the Coble creep with a grain boundary diffusion component for three different values of σ where *p′* is held constant.

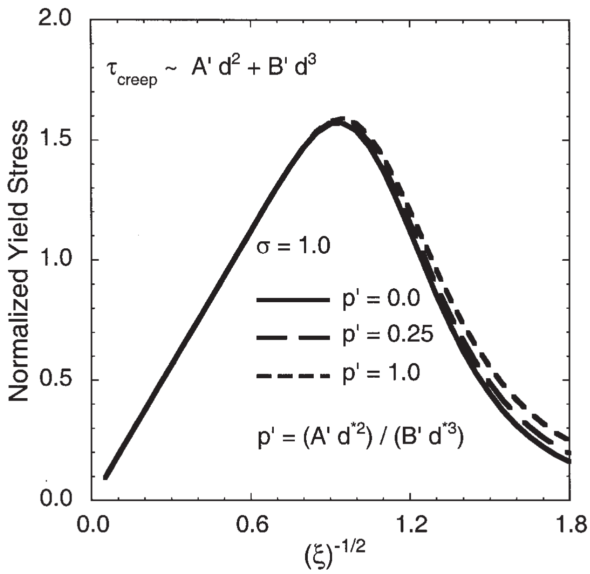

Fig. 4. Normalized yield stress as function of $\xi^{-1/2}$ for the Coble creep with a grain boundary diffusion component for three different values of *p′* where σ is held constant. Note that *p′* has minimal effect on the yield stress response.

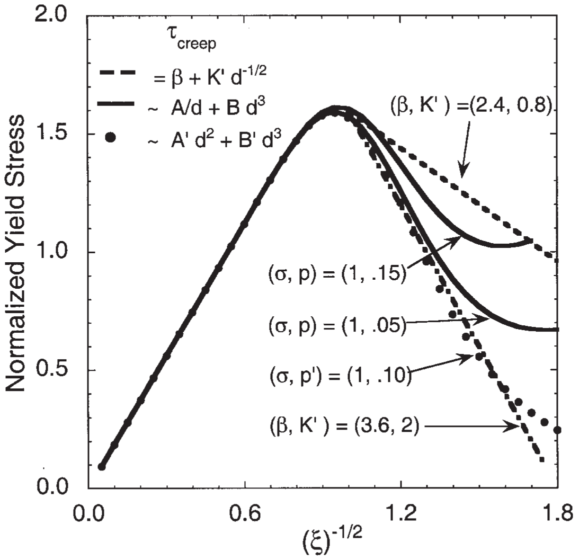

Fig. 5. Normalized yield stress as function of $\xi^{-1/2}$ comparing the various formulation of creep response for copper. The parameters β and *K′* are obtained from the experimental data.

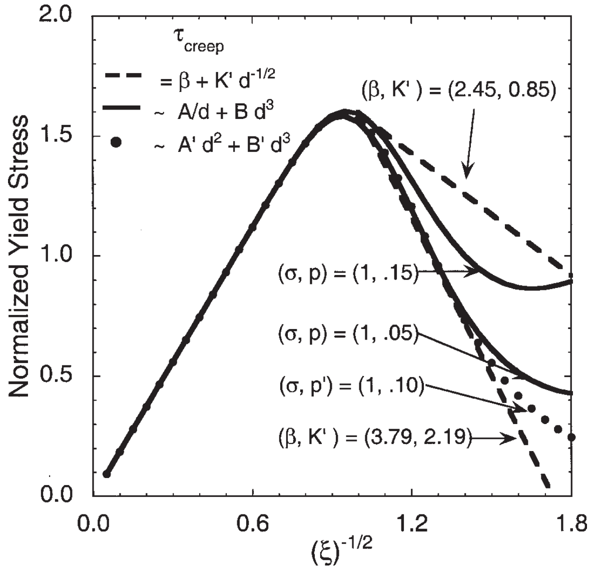

Fig. 6. Normalized yield stress as function of $\xi^{-1/2}$ comparing the various formulation of creep response for palladium. The parameters β and *K′* are obtained from the experimental data.

plot can answer the question which of the two Coble Creep expression leads to more accurate predictions.

There is however one other way to decide this question and that is by checking which of the two versions are consistent with the experimental finding of Chokshi *et al.* [20]. This is done in Fig. 5 for copper and in Fig. 6 for palladium. The dotted curve represents equation of Chokshi *et al.* [20], Eq. (7) for both copper and palladium. The values of β and *K′* are obtained by combining their formulation for yield stress and the experimental data of for copper [20] and for palladium [5, 20]. A range of 9 to 25 nm of average grain diameters was selected. From this range and assuming that Eq. (7) is valid only in the creep regime, e.g, $(d^*/d)^{-1/2} > 1$, the values of β and *K′* are determined for both the copper and palladium experimental data.

In Figs. 5 (copper) and 6 (palladium), both forms of the creep dependence on the inverse square root of the normalized grain size is shown along with Eq. (7). For the σ selected, since the effect of *p′* given by the formulation of Yamakov *et al.* [16] is minimal on overall yield stress response, only one value is shown. The Coble creep expression developed with a threshold stress gives a better fit unless the values of *d** are relatively small.

It should however be noted that the experimental result of Chokshi *et al.* [20] is some what controversial (see references [24] and [25]) and hence the comparison given here is some what tentative and further experimental results are needed to obtain a definite choice of the Coble creep expression.

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REFERENCES

[1] E. O. Hall // *Proc. Phys. Soc. London* **B64** (1951) 747.
[2] N. J. Petch // *J. Iron Steel Inst.* **174** (1953) 25.
[3] R. A. Masumura, P. M. Hazzledine and C. S. Pande // *Acta mater.* **46** (1998) 4527.
[4] C. S. Pande, R. A. Masumura and R. W. Armstrong // *Nanostructured Materials* **2** (1993) 323.
[5] P. G. Sanders, J. A. Eastman and J. R. Weertman // *Acta Mat.* **45** (1997) 4019.
[6] J. C. M. Li and Y. T. Chou // *Met. Trans.* **1** (1970) 1145.
[7] T. E. Mitchell, S. S. Hecker and R. L. Smialek // *Phys.Stat. Sol.* **11** (1965) 585.
[8] R. W. Armstrong and A. K. Head // *Acta Met.* **13** (1965) 759.

[9] C. S. Pande and R. A. Masumura, In: *Proc. of Sixth International Conf. on Fracture* (1984) P.857.

[10] N. Louat // *Acta Met.* **33** (1985) 59.

[11] A. G. Evans and J. P. Hirth // *Scripta Met*. **26** (1992) 1675.

[12] A. Lasalmonie and J. L. Strudel // *J. Mat. Sci.* **21** (1986) 1837.

[13] C. S. Pande and R. A. Masumura, In: *Processing and Properties of Nanocrystalline Materials* , ed. by C. Suryanarayana, J. Singh and F. H. Froes (Warrendale, PA, TMS,1996) p.387.

[14] Y.T. Chou // *J. App. Physics* **38** (1967) 2080.

[15] G. Szego, *Orthogonal Polynomials Americal Mathematical Society* (Colloquium Publications 1939) vol 23.

[16] V.Yamako, D. Wolf, S.R.Phillpot and H. Glieter // *Acta mater.* **50** (2002) 61.

[17] Z. Valiev, E. V. Kozolv, Yu. F. Inanov, J.Lian, A.A.Nazarov and B.Brandelet // *Acta Material* **42** (1994) 2467.

[18] G. A. Malygin // *Phys. Solid State* **37** (1995) 1248.

[19] V. G. Gryaznov, M. Yu. Gutkin, A. E. Romanov and L. I. Trusov // *J. of Mater. Sci*. **28** (1993) 4359.

[20] A. H. Chokshi, A. Rosen, J. Karch and H. Gleiter // *Scr. Metall.* **23** (1989) 1679.

[21] T. G. Nieh and J. Wadsworth // *Scripta Metall.* **25** (1991) 955.

[22] K. J. Kurzydlowski // *Scr. Met.* **24** (1990) 879.

[23] S. M. L. Sastry, private communication, 1997.

[24] H. V. Swygenhoven, M. Spaczer, A. Caro and D. Farkas // *Phys. Rev B* **60** (1999) 22.

[25] H. V. Swygenhoven and A. Caro // *Phys. Rev B* **58** (1998) 11246.