Designing nanomaterials mechanical properties from the observable nanostructure features

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ABSTRACT

Recent findings report that both mean grain size and dispersion should be used to design nanomaterials with desired mechanical properties. Grain size deals with "equivalent radius" that assumes that grains are spherical. But two grains of the same size might be different shape-wise, and hence, may impart different mechanical effects on neighbouring grains. Consequently some nanomaterials having same mean grain size and same dispersion have different properties. This paper proposes an approach to predict or design nanomaterials mechanical properties from observed features on their grains. Grain growth effect the change from one state to another. The model is tested with data from nano-Aluminium.
Relationships between statistics of microscope-observed (cumulative) number of faces on grains, density of grains in nanomaterials and mechanical properties are "similar" to Hall-Petch-to-Reverse-Petch relations. Further refinement with grain density constant may lead to no/retarded RHPR.

***Keywords*:** features per grain, cumulative features on grains, mechanical properties

1. INTRODUCTION

Nowadays, nanomaterials are mostly characterised by using three basic features of their grain; which are the sizes of grains or sizes of Grain Boundaries (GB), number of sides or triple junctions per grain and the number of faces per grain, [1-11]. The universally acceptable fact is that, [1,12,13], nanomaterials have more enhance properties due to the "reduced" nature of the above mentioned features i.e. fine mean grain sizes (grain size and GB size evolutions are inversely related), smaller mean number of triple junctions on grains, smaller mean number of faces on grains and larger GB sizes. But the irony is that only the grain size has been highly publicised as a means of relating/modelling nanomaterials mechanical properties with/from the grain features through the Hall-Petch to Reverse-Hall-Petch Relationships (i.e. HPR to RHPR). But the grain size alone does not convey all the information about the grains in nanomaterials. In fact, the grain size deals with "equivalent radius" that assumes that the grains are spherical. In reality, the grains in nanomaterials have different/random sizes, elongations, orientations, contact angle at a triple junction, number of vertices (or triple junctions), and number of faces; which all combine to determine the grains' shapes. Thus, two grains of the same size might be different in their shapes and, hence, may response differently to the applied load on the entire nanomaterials or may impart different mechanical effect on the neighbouring grains. As such, although it has been found out, [12,13], that both mean grain size and grain size dispersion (i.e. all grain size distribution statistics) should be simultaneously used in designing nanomaterials with desired properties, it has equally been observed, [12,13], that two nanomaterials from the same sample type having the same mean grain size and the same grain size dispersion may have different mechanical properties. This may be due to the differences in the shapes of the grains. Thus, a model of nanomaterials mechanical properties that uses more grain features should be an improvement or should more closely represent the information about the relationship. It must be remarked that the assertion here is not that the distribution of grain shape in nanomaterials should be used alone as a means of designing mechanical properties. This is because it is evident that two grains of similar/identical shape might be completely different: e.g. one being of the order of nanometre and the other of few orders of micrometres.

To resolve the above issue, the approach adopted in this present paper is to extend a model for mechanical properties dependent on grain size to include another model for the relationship between the observed (cumulative) features on grains. The two models are then analysed simultaneously. Thus, the extension induces the relationships between mechanical properties and the number of features per grain as well as the total number of features on all the grains. The number of features per grain is the grain's contact number, which is the number of neighbouring grains to that particular grain. Thus, the present approach that deals with features per grain or cumulative features on all the grains accommodates, more closely, all the mechanical quantities imparted by that grain unto its neighbours. Other parameters used in characterising nanomaterials, such as density of grains, are dealt with.

Since the grains in nanomaterials tend to grow when exposed to temperature more than one-third of their "melting" temperatures, the number of features on grain "evolves" too. Thus, the temporal evolution of the features

on grains affects the nanomaterials mechanical properties. The impacts of grain growth on the (cumulative) features on grains have been dealt with elsewhere, [1-11, 14-15]. The subject matter of the present paper is the impact of the evolution of the grains' features on mechanical properties.

2. METHOD

Let $\sigma_0^{'} = \sigma_0 + K_t$ be the conventional material yield stress, $A = K_d$ be Hall-Petch Relationship proportionality constant, $B = K_t[2hH_m / RT_r]$, $C = K_d[2hH_m / RT_r]$, K_t be a constant, h be atomic diameter, H_m be conventional material melting enthalpy, R be ideal gas constant, T_r be room temperature, $K_d > 100K_t$ and $\sigma_0 > 10K_t$, then the relationship between grain size and the grain yield stress in a nanomaterials undergoing a plastic deformation is given by, [1,12,13,16],

$$\sigma(\mathbf{r}) = \sigma_0^{'} + A\mathbf{r}^{-1/2} - B(\mathbf{r}^{-1/2})^2 - C(\mathbf{r}^{-1/2})^3 \qquad (1)$$

A modified model of grain growth that includes curvature-driven Grain Boundary Migration (GBM) and misorientation-angle-driven Grain Rotation Coalescence (GRC) mechanisms is given, [14,15], by

$$dr = M(r,T)\left(\frac{1}{r_c} - \frac{1}{r}\right)dt + D\sqrt{r}\,dW_e(t) + (1+a)r\,dN(t) \qquad (2)$$

where $M(r,T)$ is GB mobility function which is dependent on grain size r and the annealing temperature T, r_c is local critical grain size which is the size of the grain that neither grows nor shrinks at that particular time, D and a are constants, $dW_e(t)$ is increment of the Wiener process and $dN(t)$ is the number of coalescence events within an infinitesimal time interval dt.

Using the various models of grain growth dependent on the different grains' features, [6-11,14-15], and the Ito's differential Rule for stochastic variables, [17], the relationships between the grain size and other grains' features have been established, [18], to given by

$$\frac{M_b}{2\pi\left[1+\frac{1}{\Lambda}\right]}\left(2\pi - s[\pi - 2\theta]\right) = 2M(r,t)\left(\frac{r}{r_c} - 1\right) + D^2 r + \left(3 + 4a + a^2\right)r^2\mu + const_1 \qquad (3.1)$$

$$\frac{3}{4\pi}k_F\left(F - F_0\right) = 3M(r,T)\frac{r^3}{r_c} + 3r^2(D^2 - M(r,T)) + \left(7 + 12a + 6a^2 + a^3\right)r^3\mu + const_2 \qquad (3.2)$$

where M_b is the reduced GB mobility which is the product of GB mobility with GB surface tension, Λ is the product of the triple junction mobility and the grain size divided by the GB mobility and θ is the contact angle at a triple junction, s is the number of sides per grain, k_F is a diffusion term, F is the number of faces of a grain, μ is the rate of coalescence events of grain during grain growth and $const_i$ are the constants of integration, $F_o = \langle F^2 \rangle / \langle F \rangle$, [10,18], is called the critical number of faces per grain which is the number of faces that a grain that possesses it does not grow nor shrink at that instant. Note that F_0 varies as grains grow.

The statistics of the cumulative features on grains in nanomaterials is given by, [18-20],

$$\mathbf{E}\left[dF_p(r)\right] = \mathbf{E}\left[F_i(r)\right]v(r)dr \qquad (4.1)$$

$$\mathbf{E}\left[\left\{dF_p(R)\right\}^m\right] = \mathbf{E}\left[\left\{F_i\right\}^m\right]v(R)dR \qquad (4.2)$$

where $F_p(r)$ is the number of features of **all the** grains (i.e. cumulative features) in nanomaterials, $F_i(r)$ is the number of features **per** grain, $v(r)$ is the mean occurrence rate of grains or mean grain population density (or sparseness) and r is a "size" term .

3. RESULT

Normally, expressions (1)-(4) should be solved simultaneously using lognormal distribution of grain size, [21], and number of features per grain, [22,23]. But due to the fact all the parameters found in expression (3) are not constant and, furthermore, that from the literature search the time evolution of those parameters during grain growth were not found or are not yet known, the simplified version of the relationship between F and r obtained from experiments is used. This simplified version is given by, [8-11,18], $F = (r_0 - 1) + r/r_0$ with $r_0 = 3$, which is not made up of all the parameters in expression (3). The density of grains is given by, [18,20], $v(r).\alpha.v(F) = \lambda' e^{\beta\{3-\langle F\rangle\}}$, where $\lambda`$ is the maximum density and β is constant.

The model was tested with data from nanocrystalline aluminium sample with $\lambda`$=7000, [18], β=0.3554, [18], $H_m(\infty) = 10.71\,\mathrm{KJmol}^{1}$, [24,25], $T_m(\infty) = 933.47$ K, [24,25], $h_0 = 0.25\,\mathrm{nm}$, [24,25] and $\sigma_0^{'} = 16.7MPa$, [24,25], $K_t = 1.3$, [12,13], $T_r = 300$ K, R=8.31JK^{-1}mol^{-1}, $\sigma_0 = 15.40MPa$, [12,13], $K_d = 1301.77MPa\_nm^{1/2}$, [26], $M_0^{'} = 0.0\,\mathrm{lnn^2s^{-1}}$, [14,15], $a = -0.90$, [14,15], $D = 10^{-4}$, [14,15], $< r_c > = 1.95 < r >$, [14-15,27-28]. The rate of coalescence events of grains has been established, [14], to be $\mu(r,t) = CC\left\langle 1/r^m \right\rangle$ where CC=12 and m depends, [29], on the type of accommodation mechanism under consideration (e.g. $m=5$ for accommodation by GB diffusion and $m=4$ for accommodation by dislocation

motion or lattice diffusion). *m=4* is used. The results are presented in the plots below.

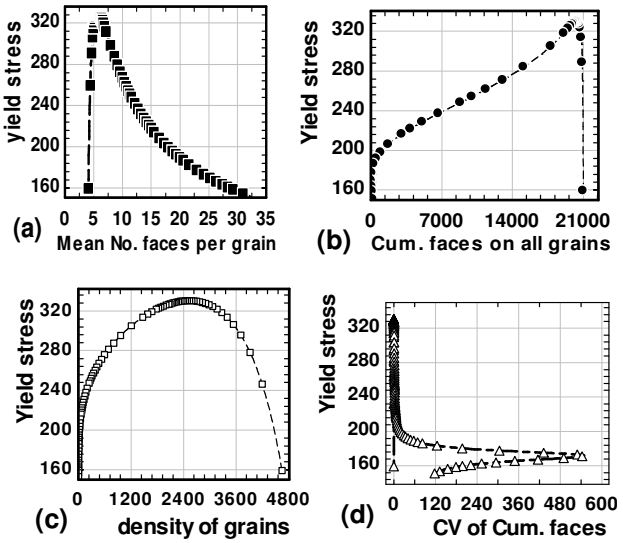

Fig. 1: Dependence of yield stress on (a) mean number of faces per grain, (b) cumulative faces on all grains, (c) grain density and (d) dispersion of cumulative faces on grain.

It can be observed that results reveal responses most of which are "similar" to HPR-to-RHPR. Using number of faces per grain as the microscope-observed features on grains, it is revealed that nanomaterials mechanical properties initial increases with increasing mean number of faces per grain and quickly reaches a maximum value at some critical mean number of faces per grain (i.e. between 5-10 mean number of faces per grain) beyond which the properties decreases slowly with increasing mean number of faces per grain, fig. (1a). Similar results are also obtained when modelling the mechanical properties from the knowledge of the cumulative number (sum) of faces on all the grains in the nanomaterials, fig. (1b). The critical mean number of faces per grain is closer to the smallest mean number of faces per grain while the critical cumulative number of faces on all the grains is closer to the largest number of faces that all the grains can possess. The shape of the plot of the mechanical properties obtained from modelling using mean number of faces per grain is highly identical to that obtained using mean grain size. This is due to the direct proportionality relationship between grain size and the number of faces per grain. The relationship between nanomaterials mechanical properties and the density of grains in the materials is also revealed, figure (1c). Careful observation of figure (1c) indicates that the data is highly clustered for materials with least number of grains (approximately conventional materials). This indicates that within the region of Reversed-Hall-Petch Relation (i.e. within the range of length scale belonging to RHRP), a slight decrease in the number of grains in nanomaterials impart a significant change in the mechanical properties of the materials. Thus, it can be anticipated that during the fabrication of nanomaterials, as the mechanical properties starts decreasing with decreasing mean features per grain, further production of new grains does not improve the situation. Thus, further improvement of nanomaterials mechanical properties may be achieved by refining other parameters used in characterising the nanomaterials while trying to maintain the grain's number density constant. The correlation between the evolution of the dispersion CV) of the cumulative features and the mechanical properties is also revealed, figure (1d). Though, it has been anticipated that there may be a direct relationship or correlation between nanomaterials mechanical properties and the dispersion (CV) of the cumulative number of faces on all the grains, [18], it is observed in fig. (1d) that the relationship between the dispersion of the cumulative features and the mechanical properties is not imminent. Thus, using the dispersion of the cumulative features alone to predict or design nanomaterial mechanical properties will not be helpful. Hence, the statistics of the distribution of the cumulative features cannot be used alone to predict or design nanomaterials mechanical properties.

4. CONCLUSION

It can be concluded that another approach to interpret and design nanomaterials mechanical from microscopic observation of nanostructures features has been proposed.

It is observed that the responses are somehow similar to the Hall-Petch Relation to Reversed Hall-Petch Relationship (i.e. HPR to RHPR).

It has also been found that that within the range of length scale leading to RHPR, if some of the parameters used in characterising nanomaterials are somehow maintained constant while others are further refined then the RHPR may not appear, i.e. nanomaterial weakening will not occur.

It has been observed that all the parameters of the distribution of the cumulative features should be used simultaneously to predict or design nanomaterials mechanical properties.

Since the number of faces per grain represents the grain's contact number, which is the number of neighbouring grains to that grain, it can be concluded that the present approach that incorporates the number of features per grain accommodates, more closely, all the mechanical quantities or effects imparted by that grain unto its neighbours and hence, on the overall nanomaterial.

It must be emphasized that more (accurate) results or dependences could have been obtained if expression (3) was used as it is, and not its approximation.

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