Rev.Adv.Mater.Sci. 10 (2005) 320-324

STRENGTH AND TOUGHNESS OF MICRO- AND NANO-STRUCTURED MATERIALS: UNIFIED INFLUENCE OF COMPOSITION, GRAIN SIZE AND STRUCTURAL DIMENSION

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Received: May 10, 2005

Abstract. Strength (or hardness) and toughness of micro- and nano-structured grained materials are analysed, assuming the key role played by the interfaces. A new fractal approach is developed to unify the influences on the mechanical properties of volumetric grain content, grain size and structural dimension. In particular, the finding of grain size effect on material strength represents an extension of the well-known empirical Hall-Petch law. A fractal structural parameter, representing an extension of the Gurland's structural parameter, is proposed to investigate, design and optimise new materials. An experimental comparison on Poly-Crystalline Diamond and WC/Co alloy concludes the paper.

1. INTRODUCTION

The relation between the macroscopic mechanical properties and the micro- or nano-structure of materials is becoming of increasing interest, playing a fundamental role in the design of new composites for high-tech applications.

Indicating with σ_C the strength of a micro- or nano-structured material, which is composed by a matrix having strength $\sigma_C^{(matrix)}$ and grains with volumetric fraction ν and strength $\sigma_C^{(grain)}$, the simplest rule of mixture would predict $\sigma_C \approx (1-\nu)\sigma_C^{(matrix)} + \nu\sigma_C^{(grain)}$. Furthermore, according to the well-known Hall-Petch law $\sigma_C - k \propto d^{-1/2}$ where d is the mean grain size (and k is a constant). Finally, according to Fracture Mechanics, in the common statistical assumption of largest crack length proportional to the characteristic structural size R, it results $\sigma_C \propto R^{-1/2}$. The aim of this paper is the generalization and unification of the previous influences, of composition ν, grain size d and structural dimension R, not only for strength but also for fracture toughness. A fractal structural parameter, representing an extension of the Gurland's structural parameter [1], is proposed to design new materials as a compromise optimisation of strength and fracture toughness.

2. ENERGY SCALING

To predict the influence of grain size, structural dimension and volumetric grain content in a unified manner, a fractal approach is herein considered. Accordingly, we assume a fractal (or self-similar) distribution of grains, for which the probability density function $p(r)$, describing their distribution in size r, has to be written as [2,3]:

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$$p(r) = D\frac{r_{\min}^{D}}{r^{D+1}}, \tag{1}$$

where $D=3\gamma$ is the fractal exponent (usually comprised between 2 and 3) and $r_{\min}$ is the size of the smallest grain. The case of a Gaussian distribution is also treated at the end of the section, as an example of different grain size distribution.

The main assumption of the theory is that we assume a key role to be played by the interfaces. In particular, we assume that the energy dissipation W connected to the presence of the grains takes place at the interfaces and thus is statistically proportional to their surface area S_g [2,3], i.e.:

$$W \propto S_g \propto \int_{r_{\min}}^{r_{\max}} r^2 dN \propto \int_{r_{\min}}^{r_{\max}} N_0 r^2 p(r) dr \propto N_0 r_{\min}^2, \tag{2}$$

where $r_{\max}$ is the size of the largest grain ($r_{\max}>>r_{\min}$) and N_0 is the total number of grains. On the other hand, the total volume V_g of the grains is:

$$V_g \propto \int_{r_{\min}}^{r_{\max}} r^3 dN \propto \int_{r_{\min}}^{r_{\max}} N_0 r^3 p(r) dr \propto N_0 r_{\min}^{D} r_{\max}^{3-D}. \tag{3}$$

Deriving the expression of N_0 from the previous equation and putting it into Eq. (2), yields:

$$W \propto V_g r_{\min}^{2-D} r_{\max}^{D-3}. \tag{4}$$

As a consequence, the energy dissipated (at the interfaces) per unit volume V of material is:

$$W_c = \frac{W}{V} \propto \nu r_{\min}^{2-D} r_{\max}^{D-3}, \tag{5}$$

where $\nu = V_g / V$ represents the volumetric fraction of grains.

Assuming the statistical self-similarity hypothesis, i.e., $r_{\max} \propto \sqrt[3]{V_g}$ (the larger the total grain volume, the larger the largest grain [2,3]), the effect of the structural size (size effect) can be obtained as:

$$W_c \propto v^{\gamma} r_{\min}^{2-D} V^{\frac{D-3}{3}}. \tag{6}$$

Usually $r_{\min}$ is assumed to be a constant, i.e., a material property. The mean value of the surface of grains, proportional to $\langle r^2 \rangle$, as well as of their volume, proportional to $\langle r^3 \rangle$, are substantially estimated in Eqs. (2) and (3). On the other hand, the evaluation for the mean value of the grain size r gives:

$$\langle r \rangle \propto \frac{1}{N_0}\int_{r_{\min}}^{r_{\max}} r dN \propto \int_{r_{\min}}^{r_{\max}} r p(r) dr \propto r_{\min}. \tag{7}$$

Introducing $D=3\gamma$ and Eq. (7) into Eq. (6), noting that $V \propto R^3$ with R structural size, and $d \propto \langle r \rangle$ being the grain size, we can write:

$$W_c \propto \nu^{\gamma} d^{2-3\gamma} R^{3(\gamma-1)} \tag{8}$$

that represents the scaling law of the energy density dissipated at the interfaces.

Note that if $D<2$ in Eq. (1), $\gamma=2/3$ in Eq. (8), whereas if $D>3$ in Eq. (1), $\gamma=1$ in Eq. (8), see [2]. We will show now how such a result is more general than expected. In particular, we will show that, assuming a Gaussian distribution for the grain sizes, the energy density scales as predicted by the fractal approach in the limit case of $\gamma=1$. Accordingly, we assume a Gaussian (or normal) distribution of grains, for which the probability density function is $p(r) = \frac{1}{\sqrt{2\pi}\sigma} e^{-\frac{(r-r_m)^2}{2\sigma^2}}$, where σ is the standard deviation and $r_m \equiv \langle r \rangle$ is the mean grain size, $r_m = \frac{1}{N_0}\int_0^{\infty} r dN = \int_{-\infty}^{\infty} r p(r) dr$. Note that the integrals evaluated between minus infinite and zero must give negligible contributions to the final results, the variable r being defined as positive. The energy dissipation W connected to the presence of the grains is statistically expected to be proportional to their surface area, i.e.,

$$W \propto S_g \propto \int_0^{\infty} r^2 dN = \int_0^{\infty} N_0 r^2 p(r) dr = N_0 (r_m^2 + \sigma^2).$$

On the other hand, the total volume of the grains is

$$V_g \propto \int_0^{\infty} r^3 dN = \int_0^{\infty} N_0 r^3 p(r) dr = N_0 (r_m^3 + 3 r_m \sigma^2).$$

Eliminating N_0 from the previous equations, being $r_m \propto d$, yields asymptotically $W \propto V_g d^{-1}$. As a consequence, the energy dissipated per unit volume of material becomes $W_C \propto \nu d^{-1}$, identical to Eq. (8) if $\gamma=1$.

3. STRENGTH AND FRACTURE TOUGHNESS SCALING

Eq. (8) represents the unified law to evaluate the grain and structural size effects as well as the influence of the volumetric grain content on dissipated energy density. Noting that the square root of the energy dissipated due to the presence of the grains per unit volume of material (if we assume negligible size effects on the elastic modulus) can be considered to be proportional to the strength of the grains

(not intrinsic, but in the matrix) [4], coupling Eq. (8) with a classical rule of mixture gives the following unified scaling law:

$$\sigma_c^{(grain)} \approx k_\sigma \nu^{\frac{\gamma}{2}} d^{1-\frac{3}{2}\gamma} R^{\frac{3}{2}(\gamma-1)}, \tag{9a}$$

$$\sigma_c = (1-\nu)\sigma_c^{(matrix)} + \nu\sigma_c^{(grain)}, \tag{9b}$$

where k_σ is a constant. More complex rules of mixture could be also considered [5,6]. We note that Eq. (9a) represents an extension, including the structural size, of the Gurland structural parameter [1], that is an extension, including the volumetric grain content, of the Hall-Petch relationship for grain size effect on material strength. Thus, for hardness $H \propto \sigma_C$ (or wear resistance) the same scaling is expected.

An approximated law can be also proposed for fracture toughness. According to Griffith, if the characteristic crack length is l, $K_{IC}^{(grain)} \propto \sigma_C^{(grain)} \sqrt{l}$. Two plausible hypotheses for l are $l \propto R$ or $l \propto d$; thus, in general, we can assume $l \propto d^{1-2\alpha} R^{2\alpha}$ where $0<2\alpha<1$ is a constant. Accordingly, coupling this law with Eqs. (9) and with a classical rule of mixture yields:

$$K_{IC} \approx (1-\nu)K_{IC}^{(matrix)} + \nu K_{IC}^{(grain)}, \tag{10a}$$

$$K_{IC}^{(grain)} \approx k_K \sigma_c^{(grain)} d^{1/2-\alpha} R^{\alpha}, \tag{10b}$$

where k_K is a constant and $K_{IC}^{(matrix)}$ is the fracture toughness of the matrix.

4. FRACTAL STRUCTURAL PARAMETER AND DEVIATION FROM THE HALL-PETCH REGIME

The Hall-Petch relationship has been used for several decades to describe the relationship between strength and grain size, namely:

$$\sigma_c - k \propto d^{-1/2}. \tag{11}$$

It is interesting to observe that a deviation of the exponent from that of the Hall-Petch relationship occurs [7]. The experiments on fine grained micro- and nano-structured materials seem in fact to suggest three different regions for the negative exponent of the Hall-Petch relationship:

(1) a region from single crystal to a grain size of about 1μm, where the exponent seems to be close to 1/2;
(2) a region for grain sizes ranging from about 1 mm to 30 nm, showing exponents lower than 1/2;
(3) a region below a very small critical grain size (of about 30 nm), with an exponent nearly equal to zero.

The fractal approach is able to justify the empirical law of Hall-Petch, as well as the deviation of its exponent, which is observed to be close to zero at small size scales and to -1/2 at larger size scales. The inversion of the Hall-Petch law, formally described by positive exponents, still remains a not fully understood phenomenon.

The predictions of the fractal approach for strength (or hardness) and for the fracture toughness are described by Eqs. (9) and (10). Accordingly, we can define a Fractal Structural Parameter FSP:

$$FSP = \nu^{\frac{\gamma}{2}} R^{\frac{3}{2}(\gamma-1)} d^{1-\frac{3}{2}\gamma} \tag{12}$$

as an extension of the Gurland's structural parameter [1].

Previous investigations on grain size distributions [3] seem to suggest that $\gamma=2/3$ (surface effects prevail) at small scales, as well as $\gamma=1$ at large scales (volume effects prevail). These limit cases correspond respectively to $FSP \propto \nu^{1/2} R^{-1/2} d^{0}$ or $FSP \propto \nu^{1/2} R^{0} d^{-1/2}$. Since $\sigma_C \propto k+FSP$, this reproduces exactly the discussed deviation of the exponent in the Hall-Petch law.

5. EXPERIMENTAL ASSESSMENT AND MATERIAL DESIGN

Let us consider that the structural size effects predicted by Eqs. (9) and (10) agree with the experiments satisfactorily [4], so that we are herein more interested in the effects of size and volumetric content of grains. We can rewrite Eqs. (9) for strength (or hardness) as:

$$y = \frac{\left(\sigma_C - (1-\nu)\sigma_C^{(matrix)}\right) R^{\frac{3}{2}}}{\nu d} = k_\sigma \left(\nu^{\frac{1}{2}} R^{\frac{3}{2}} d^{-\frac{3}{2}} \right)^{\gamma} = k_\sigma x^{\gamma}. \tag{13a}$$

Therefore, the fractal approach predicts a power-law between the auxiliary variables y and x, with the exponent γ comprised between 2/3 and 1. This is equivalent to verify the validity of the FSP-based approach. The advantage here is that the exponents γ, as well as the constant of proportionality k_σ, can be easily obtained as best fit parameters.

When the material strength is predicted and γ determined, then the fracture toughness can be also estimated by Eqs. (11), as a best fit of:

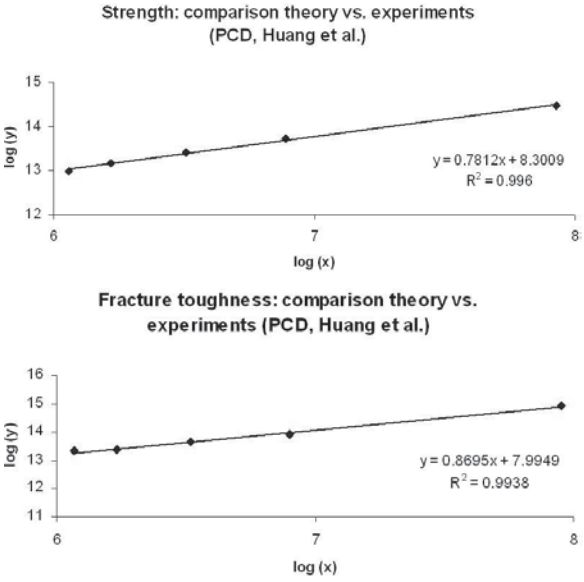

Fig. 1. (a) Experimental assessment: PCD strength (Eq. (13a); [8]). (b) Experimental assessment: PCD toughness (Eq. (13b); [8]).

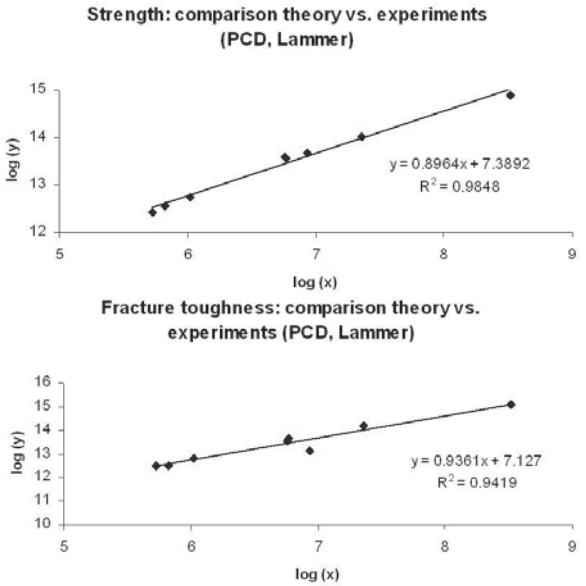

Fig. 2. (a) Experimental assessment: PCD strength (Eq. (13a); [9]). (b) Experimental assessment: PCD toughness (Eq. (13b); [9]).

$$y = \frac{\left(K_{IC} - (1-\nu)K_{IC}^{(matrix)}\right)R^{\frac{3}{2}}}{\nu^{1+\frac{\gamma}{2}}d^{\frac{3}{2}}}$$
$$= k_K k_\sigma \left(R^{\frac{3}{2}} d^{-\frac{3}{2}}\right)^{\gamma+\frac{2}{3}\alpha} = k_{K\sigma} x^{\gamma+\frac{2}{3}\alpha} \qquad (13b)$$

on the parameters $K_{k\sigma}$,α.

We refer to the experimental investigation on fine grained PCD materials [8,9] and on WC-Co alloy [1], neglecting the inversion of the Hall-Petch law observed at small scales for WC/Co [1].

In Fig. 1, the experimental assessment of the fractal theory according to Eqs. (13) (setting the structural size arbitrarily equal the unity; all the parameters are expressed in [SI] units) is presented for the strength and toughness of PCD, deduced by fitting the experimental data in [8]. Such experiments strongly confirm the prediction of the fractal approach. The exponent $\gamma \approx 0.78$ for the considered material is found belonging to the theoretical range [2/3,1]; note that from the best fit we have deduced $2\alpha \approx 0.27$, and as expected it is $0<2\alpha<1$. The corresponding laws for the PCD are fitted as follows:

$$\sigma_c(d,\nu) \approx$$
$$(1-\nu)\sigma_c^{(matrix)} + 200\times 10^6 \times \nu^{1.38} d^{-0.17}, \qquad (14a)$$

$$K_{IC}(d,\nu) \approx$$
$$(1-\nu)K_{IC}^{(matrix)} + 100\times 10^6 \times \nu^{1.38} d^{-0.18} \qquad (14b)$$

in [SI] ($\sigma_c^{(matrix)} \approx 500$MPa, $K_{IC}^{(matrix)} \approx 20\text{MPa}\sqrt{\text{m}}$). Similar results are obtained by fitting the PCD experiments described in [9], as reported in Fig. 2, or on WC/Co alloy [1], as reported in Fig. 3.

In addition, considering a reference PCD material with grain size d_r and volumetric content ν_r, we can deduce the increments in the strength (or hardness $H \propto \sigma_C$) and fracture toughness expected for a new PCD material, designed with different grain size d and volumetric content v. For example, for the hardness we would have to evaluate the ratio $V(H(d,\nu)-H(d_r,\nu_r))/H(d_r,\nu_r)$. The increments of the hardness and of the fracture toughness for a standard PCD ($\nu_r \approx 0.9$, $d_r \approx 30$ μm, $\sigma_c^{(matrix)} \approx 500$MPa, $K_{IC}^{(matrix)} \approx 20\text{MPa}\sqrt{\text{m}}$) are reported in Fig. 4, according to eqs. (14). This diagram can be considered an example of material optimization map. Note the small (upper) region where both the increments are positive: a new material belonging to this optimal

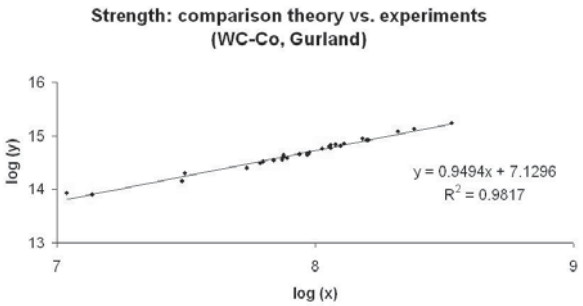

Fig. 3. Experimental assessment: WC-Co alloy strength (Eq. (13a); [1]).

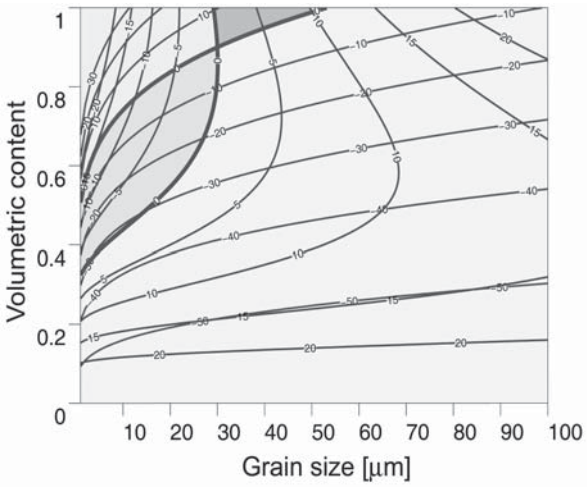

Fig. 4. Hardness and Fracture Toughness Increments %. The curves were derived according to Eqs. (14), choosing as the reference a standard PCD, described by the intersections of the two 0% curves.

region will be harder and tougher than the standard one.

6. CONCLUSIONS

A generalization of the Hall-Petch law for grain size effect on material strength was introduced by Gurland to take into account the volumetric grain content. The result of our approach is a generalization of the Gurland parameter, introducing a fractal structural parameter (FSP), in which the scaling related to the structural dimension R is also included and in which the exponents are generalized. The same approach is extended to the fracture toughness; experiments on PCD materials and WC/Co alloy seem to confirm its validity. Future works will be focused on the inversion of the Hall-Petch relationship on material strength (formally described by a fractal exponent γ lower than 2/3), which here were neglected.

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