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BIO-INSPIRED HIERARCHICAL NANOMATERIALS FOR SPACE APPLICATIONS

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In this paper we discuss the superior properties of strong/hard and simultaneously tough innovative bio-inspired hierarchical or fractal (2D-platelet-, 1D-fibre- or 0D-grained-reinforced) nanomaterials, ideal for (aero)space applications. As a practical example, we have treated recent experimental results on double cemented WC-Co, a two-level hierarchical grained material, demonstrating that hierarchy is able to increase the fracture toughness by a significant percentage.

Keywords: Nanomaterials, strength, toughness, bio-inspired, hierarchical, space

1. INTRODUCTION

Space vehicles require the use of lightweight and stiff materials with superior properties, such as strength or hardness (e.g. to reduce the erosion caused by micrometeorite impacts) and toughness (e.g. to reduce the risk of catastrophic and fatigue crack propagations). Such properties have to be preserved also at high temperature (e.g. due to atmospheric friction in the take-off and landing phases or to light photons in vehicles based on solar sails when flying near the sun).

These required properties could be simultaneously achieved in nanomaterials (e.g. [1]). In particular, biological nanomaterials exhibit several levels of hierarchy, from the nano- to the macro-scale. For instance, sea shells have 2 or 3 orders of lamellar structures, as well as bone, similarly to dentin, has 7 orders of hierarchy [2, 3]. These biological nanomaterials are composed by hard and strong mineral structures embedded in a soft and tough protein matrix. In bone and dentin, the mineral platelets are ~3 nm thick, whereas in shells their thickness is of ~300 nm, with very high slenderness. Thus Nature seems to suggest us the key for optimizing materials with respect to both strength and toughness, without losing stiffness [4, 5]. Similarly, fractal [6] grained nanomaterials could simultaneously be optimized with respect to both strength and toughness [7, 8].

Long-term and visionary nanotechnological conceptions, however, go far beyond these first approaches. This applies in particular to the development of biomimetic materials with the ability of self-organization, self-healing, and self-replication by means of molecular nanotechnology. One objective here is the combination of synthetic and biological materials, architectures and systems, respectively, the imitation of biological processes for technological applications. This field of nanobiotechnology is at present still in the state of basic research, but is regarded as one of the most promising research fields for the future. For example, due to the postulated high innovation potential for space technology, NASA invests a substantial part of its nanotechnology budget into this field of basic research. NASA at present establishes the Institute for Biologically Inspired Materials, with different university research institutes, e.g. Princeton University, as participants. This institute is funded for a period of 10 years with annually $3 million, and its main task is to transfer basic inventions to the development of materials with extraordinary mechanical and self-healing properties, like those of some biological materials such as shells or bones [9].

In this paper we discuss the superior properties of nanomaterials for (aero)space applications, but mainly only with respect to their basic properties of strength and toughness.

2. BIO-INSPIRED HIERARCHICAL NANOMATERIALS

Strength, toughness and stiffness of materials are measured by tensile tests. For this reason we limit ourselves in considering the tensile test, even if the formulation could be extended, but only in an approximated way, for different configurations, e.g. bending or twisting. Imagine a virtual tensile test on a hierarchically fibre-reinforced bar. Its cross-section, composed by hard inclusions embedded in a soft matrix, is schematized in Fig. 1 (left).

The smallest units, at the level N, are considered scale-invariant and related to the theoretical material strengths of the hard and soft phases, respectively σ_h, σ_s, where usually $\sigma_h >> \sigma_s$. Each inclusion at the level $k+1$ contains n_k smaller ones, each of them with cross-sectional area A_k. Thus, the total number of inclusions at the level k is

$$N_k = \prod_{j=1}^{k} n_j$$

The *equilibrium equation* is

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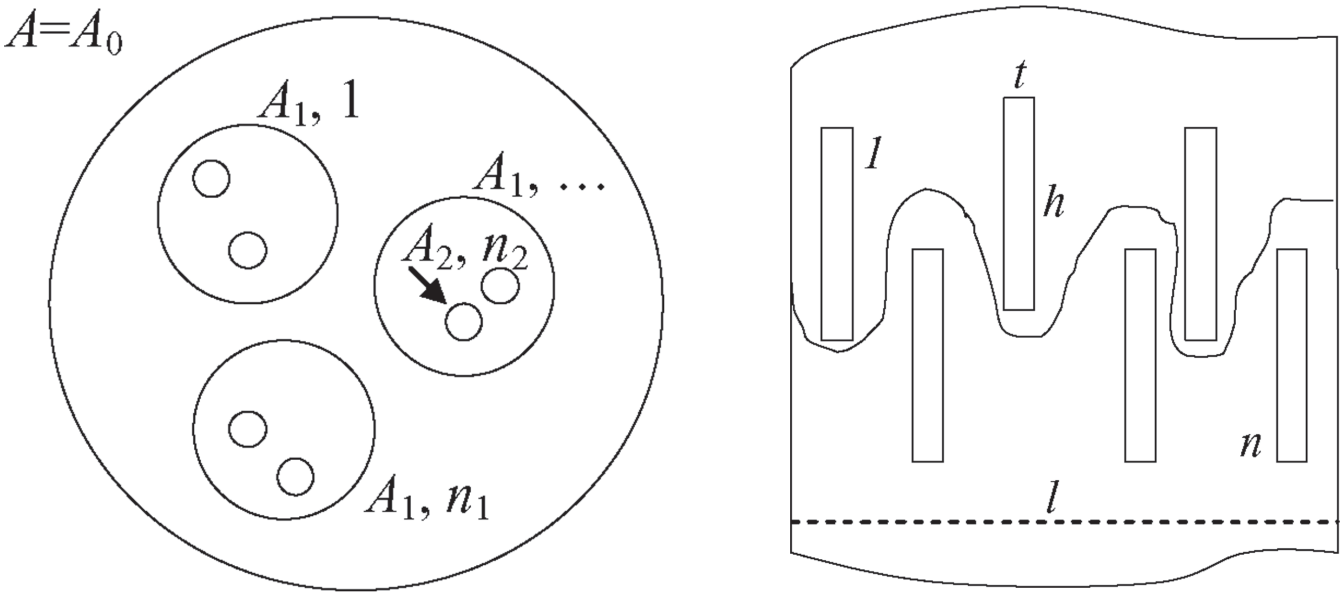

Fig. 1 The cross-section of a hierarchical bar (left) and the lateral view of the crack surface (right) corresponding to the toughening mechanism.

$$F \equiv A\sigma_C = F_h + F_s = N_k A_k \sigma_{hk} + \left(A - N_k A_k\right)\sigma_{sk}$$
$$= N_N A_N \sigma_{hN} + \left(A - N_N A_N\right)\sigma_{sN}, \forall k$$

where F is the critical applied force, F_h, F_s are the forces carried by the hard and soft phases respectively, $A \equiv A_0$ is the cross-section area of the bar, σ_C is its strength,

$$\sigma_{hN} \equiv \sigma_h, \sigma_{sk} \equiv \sigma_s \ (\forall k)$$

and the subscript k refers to the quantities at the level k. Note that

$$\varphi_k = \frac{n_{k+1} A_{k+1}}{A_k}$$

represents the cross-sectional fraction of the inclusions at the level k+1 in the inclusions at the level k.

For self-similar structures $n_k = n$ and $\varphi_k = \varphi$, thus k-independent numbers and fractions; accordingly $N_k = n^k$. Since the inclusions present a fractal distribution [6], we expect $F_h \propto R^D$ where

$$R = \sqrt{A}$$

is a characteristic size and D is a constant, the so-called "fractal exponent"; the constant of proportionality can be deduced noting that $F_h(A = A_N) = A_N \sigma_{hN}$, and thus

$$F = \sigma_{hN} R_N^{2-D} R^D$$

Accordingly, from,

$$F_h = \sigma_{hN} R_N^{2-D} R^D = \sigma_{hN} n^N R_N^2$$

we derive:

$$N = D \frac{\ln R/R_N}{\ln n} \qquad (1)$$

that defines the number of hierarchical levels that we need to design an object of characteristic size R. Eq. (1) shows that only few hierarchical levels are required for spanning several orders of magnitude in size. For example, for a nano-structured hierarchical "universe", considering for R its actual radius, i.e., $R \approx 10^{26}$ m, for the smallest units a radius on 1nm, i.e., $R_N \approx 10^{-9}$ m, n = 5 and D = 2 would result in only 100 hierarchical levels.

The scaling exponent D can be determined noting that $A - N_N A_N = A(1 - \phi)$, where $\phi = \varphi^N$ represents the macroscopic (at level 0) cross-sectional fraction of the hard inclusions. Thus, we derive $R/R_N = (n/\varphi)^{N/2}$. Introducing this result into eq. (1) provides the fractal exponent, as a function of well-defined physical quantities:

$$D = \frac{2 \ln n}{\ln n - \ln \varphi} \qquad (2)$$

Note that D represents the fractal dimension of the inclusions, i.e., of a lacunar two-dimensional domain in which the soft matrix is considered as empty [10, 11]; for example, the dimension of the well-known Sierpinski carpet (Fig. 2), is D = 1.89.

Since $\sigma_{hN} n^N R_N^2 = \sigma_{hN} R_N^{2-D} R^D$ and $R/R_N = (n/\varphi)^{N/2}$, we derive:

$$\phi = \varphi^N = (R/R_N)^{D-2} \qquad (3)$$

Thus, from the equilibrium equation a scaling of the strength is predicted:

$$\sigma_C = \sigma_h \varphi^N + \sigma_s(1 - \varphi^N) = \sigma_h (R/R_N)^{D-2} + \sigma_s(1 - (R/R_N)^{D-2}) \qquad (4)$$

Noting that $n > 1$ and $\varphi < 1$, we deduce $0 < D < 2$ and thus eq. (2) predicts that "smaller is stronger" ($\sigma_h >> \sigma_s$).

On the other hand, the *energy balance* implies

$$W \equiv AG_C = W_h + W_s = A_k G_{hk} + \left(A - N_k A_k\right) G_{sk}$$
$$= N_N A_N G_{hN} + \left(A - N_N A_N\right) G_{sN}, \forall k$$

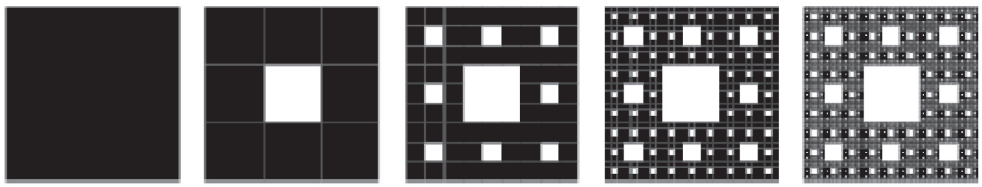

Fig. 2 The Sierpinski carpet (*D*=1.89) at different level of observation; it corresponds to a deterministic hierarchical bar in which the empty space is the soft matrix, and the complementary zones are the hard inclusions.

where W, W_h, W_s are respectively the dissipated fracture energies in the bar, hard and soft phases, and

$$G_C,\ G_{hN} \equiv G_h,\ G_{sk} \equiv G_s\ (\forall k)$$

are the fracture energies per unit area of the bar, hard and soft phases respectively; usually $G_h << G_s$. Accordingly, the fracture energy must scale as:

$$G_C = G_h\varphi^N + G_s(1-\varphi^N) = G_h(R/R_N)^{D-2} + G_s(1-(R/R_N)^{D-2}) \tag{5}$$

And thus "larger is tougher". In the next section, toughening mechanisms will be introduced in the model.

On the other hand, the *compatibility equation* implies (bars in parallel):

$$\begin{aligned} K \equiv EA = K_h + K_s &= N_k A_k E_{hk} + \left(A - N_k A_k\right) E_{sk} \\ &= N_N A_N E_{hN} + \left(A - N_N A_N\right) E_{sN},\ \forall k \end{aligned}$$

where K, K_h, K_s are respectively the "elastic" force of the bar, hard and soft phases and E, $E_{hN} \equiv E_h$, $E_{sN} \equiv E_s$ are the Young's moduli of the bar, hard and soft phases respectively. Accordingly, the Young's modulus must scale as:

$$E = E_h\varphi^N + E_s\,(1-\varphi^N) = E_h(R/R_N)^{D-2} + E_s(1-(R/R_N)^{D-2}) \tag{6}$$

Since usually $E_h >> E_s$, "smaller is stiffer".

Eqs. (4-6) show that at the smaller size-scales the inclusions are dominating, whereas at the larger size-scales the matrix dominates. These equations present the same self-consistent form: in fact, regarding the generic property X (σ_C, G_C or E) at the level N–1

$$X_{N\text{-}1} = X_h\varphi + X_s\,(1-\varphi)$$

Thus, at the level N–2

$$X_{N\text{-}2} = X_{N\text{-}1}\varphi + X_s(1-\varphi) = X_h\varphi^2 + X_s(1-\varphi^2)$$

and iterating

$$X \equiv X_0 = X_h\varphi^N + X_s(1-\varphi^N)$$

as described by eqs. (4-6). In addition, it is clear that the scaling laws predicted by eqs. (4-6) are particularly reasonable, since they predict two asymptotic behaviours for macro- and nano size-scales. Note that for a three-dimensional architecture (i.e., particle inclusions and not longitudinal fibres) for which also the third dimension plays a role, in the stiffness of eq. (6) the factor 2 must be replaced by 3, φ becomes the volume fraction rather than the cross-sectional fraction and D is deduced from eq. (2) considering again the factor 3 instead of 2; this is true if we consider valid the rule of mixture of eq. (6) also for a nonparallel architecture.

Then, the fracture toughness can be derived as

$$K_C = \sqrt{G_C E}$$

whereas the hardness $H_C \propto \sigma_C$ formally making the substitution $\sigma_C \to H_C$ in eq. (4). Note that the important equality (3) would allow us to derive scaling laws from "rules of mixture" also in different systems and for different properties, e.g., the friction coefficient.

Finally, for quasi-fractal hierarchy, described by $n(R)$ and $\varphi(R)$ weakly varying with the size R, function $D(R)$ should be considered in eqs. (4-6), as deducible from eq. (2).

According to the previous analysis, the fracture surface is assumed to be planar. On the other hand, the inclusions could serve as hard structures to deflect the crack path or as crack bridging elements. In the latter case, the inclusions will be pulled-out after fracture, incrementing the dissipated energy in a fashion similar to the former mechanism (if fracture of the matrix is assumed similar to that of the interface; it is evident that this hypothesis can be easily removed). To model such effects, we simply assume the two-dimensional scheme reported in Fig. 1 (right), which is a lateral view of the crack surface of Fig. 1 (left). According to this scheme

$$G_s^{(eff)} l = G_s\,\left(l + nh\right)$$

where l is the nominal crack length, n is the number of inclusions along l and h is their height. Noting that $\varphi = nt/l$, with t thickness of the inclusions, and that $\lambda = h/t$ is their slenderness, the effective fracture energy becomes:

$$G_s^{(eff)} = \left(1+\lambda\varphi\right) G_s \tag{7}$$

Thus, for this toughening mechanism, the fracture energy $G_s^{(eff)}$ can be even much larger ($\varphi \approx 1$; $\lambda >> 1$) than the intrinsic fracture energy of the matrix G_s. This explains why the shape of mineral crystals is found to be very anisometric (platelets, [12]): the anisometry is larger for bone and dentin (platelets 3 nm thick and up to 100 nm long) as well as for enamel (15-20 nm thick, 1000 nm long) than for nacre (i.e., see shells, 200-500 nm thick and 5-8 μm long). For details on the hierarchical bone structure see [13].

An example of a new bio-inspired hierarchical nanomaterial, based on super-nanotubes-reinforced matrix, has recently been proposed in [8], mimicking nacre to optimize the super-composite with respect to both strength and toughness.

3. FRACTAL GRAINED NANOMATERIALS

For a fractal grained material, the strength (or, equivalently, the

hardness, namely $H_C \propto \sigma_C$) and toughness can be derived as functions of the volumetric grain content ϕ, grain size d and structural dimension R [7]. In particular we found:

$$\sigma_C(\phi,d,R) = \sigma_h\phi + \sigma_s(1-\phi) \text{ with } \sigma_h = k_\sigma \phi^{\frac{\gamma}{2}} d^{1-\frac{3}{2}\gamma} R^{\frac{3}{2}(\gamma-1)} \tag{8}$$

$$K_C(\phi,d,R) = K_h\phi + K_s(1-\phi) \text{ with } K_h = k_K \sigma_h d^{\frac{1}{2}-\alpha} R^{\alpha} \tag{9}$$

where $2/3 \le \gamma \le 1$ is one third of the fractal exponent of the grain distribution, $0 \le \alpha \le 1/2$ is the self-similarity exponent (i.e., the characteristic crack length is assumed to be proportional to $d^{1-2\alpha} R^{2\alpha}$) and $k_{\sigma,K}$ are constants related to the strength and toughness of the interfaces.

For example, for a polycrystalline diamond (PCD) with standard size, that we arbitrary fix as $R = 1$, having diamond grains connected by a binder or matrix phase, by fitting extensive experimental data [14] we find for the strength σ_C and for the fracture toughness K_C the following power laws (or fractal) scalings,

$$\sigma_C(\phi,d,R=1) = 200\times10^6 \times \phi^{1.391} d^{-0.172} + \sigma_s(1-\phi)$$

$$K_C(\phi,d,R=1) = 99\times10^6 \times \phi^{1.391} d^{0.196} + K_s(1-\phi)$$

in SI units, where σ_s = 500 MPa, $K_s = 20\text{MPa}\sqrt{\text{m}}$ denote the strength and fracture toughness of the matrix. The effect of the structural dimension R is here neglected. Thus, considering a reference PCD with grain size d_r and volumetric content ϕ_r, we can deduce the increments in hardness ($H_C \propto \sigma_C$) and fracture toughness expected by using a new PCD material, designed with different grain size d and volumetric content ϕ. For example, for the hardness we would have to evaluate the ratio

$$\left[H_C(\phi,d) - H_C(\phi_r,d_r)\right] / H_C(\phi_r,d_r) \times 100\%$$

In Fig. 3, the increments of the hardness and of the fracture toughness for a standard PCD ($\phi_r \approx 0.9$, $d_r \approx 30$ μm) are reported. The experimental range for the grain size is from 5 to 90 μm, whilst that for the volumetric content is from .89 to .95; thus, large part of the graph is, strictly speaking, an extrapolation. These diagrams can be considered as a PCD optimization map. Basically, the increment in hardness is given by the increase in the volume fraction of hard phase, which counterbalances the increase in d. The increment in fracture toughness, on the other hand, is given by the rising of the grain size, which counterbalances the decrease of the ductile phase volume fraction.

4. HIERARCHICAL GRAINED NANOMATERIALS

It is evident that coupling the approaches proposed in the two previous sections is trivial and straightforwardly leads to the equations required to treat a hierarchical grained material (imagine spherical hierarchical grains as depicted in Fig. 1, left). In particular inserting $\phi = \phi^N$, $R = d_{N-1}$, $\lambda = d_{N-1}/d_N$, $k_{\sigma K} = k_\sigma k_K$ into eqs. (8, 9) yields:

$$\sigma_C = k_\sigma \varphi^{\left(1+\frac{\gamma}{2}\right)N} \lambda^{\frac{3}{2}(\gamma-1)} d^{-\frac{1}{2}} + \sigma_s\left(1-\varphi^N\right) \tag{10}$$

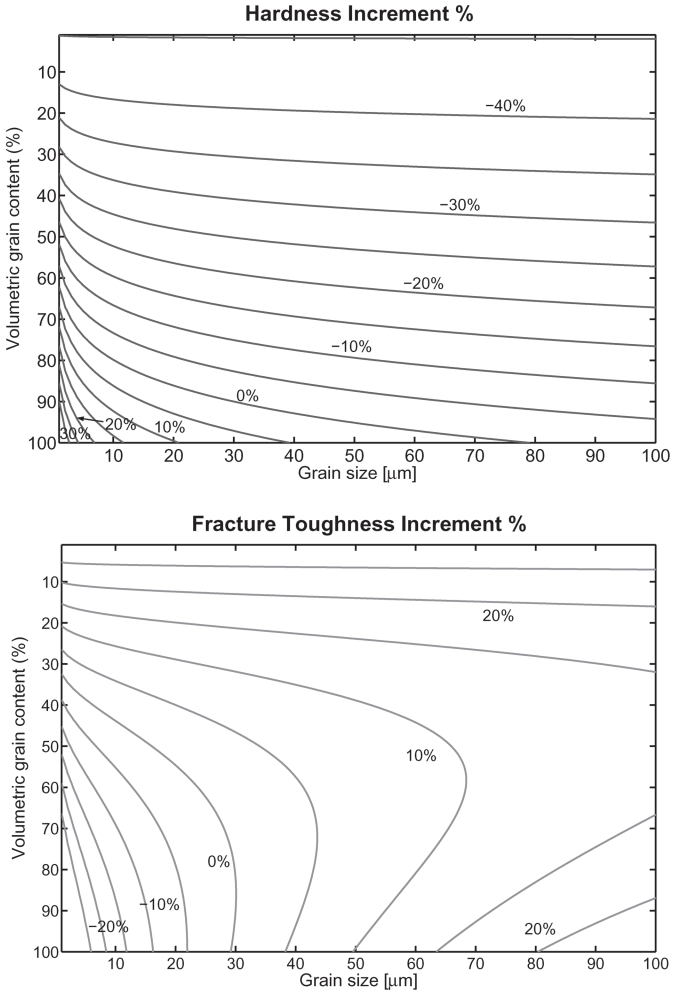

Fig. 3 Iso-hardness lines (top) and iso-toughness lines (bottom). Numbers along the curves indicate hardness and fracture toughness increments %.

$$K_C = k_{\sigma K} \varphi^{\left(1+\frac{\gamma}{2}\right)N} \lambda^{\frac{3}{2}(\gamma-1)+\alpha} + K_s\left(1-\varphi^N\right) \tag{11}$$

As an example, we can treat the experimental results on double cemented WC-Co [17], a two-level hierarchical grained material, for which $\varphi_1 = 0.73$, $\varphi_2 = 0.94$, $d_1 = 200$ μm, d_2 = 1-6 μm. Thus

$$\varphi \equiv \sqrt{\varphi_1\varphi_2} = 0.69,\ N=2,\ d = \text{1-6 μm}$$

and respectively λ = 33-200. Roughly neglecting here the role of the brittle grains in the toughness we expect a toughness 1.15 or 5.17 times larger than that of a standard WC-Co alloy having the same macro- or micro-volumetric composition. Experimental observations are in between our predictions.

5. CONCLUSIONS

The developed mathematical model, summarized in the numbered equations, allows us to preliminary design and optimize with respect to both strength and toughness bio-inspired hierarchical or fractal grained innovative nanomaterials, ideal for (aero)space applications. A significant increment in the hardness without reducing the fracture toughness would for example lead to a new class of materials with superior performances against the space debris erosion [18].

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