A top-down approach for the prediction of hardness and toughness of hierarchical materials

Alberto Carpinteri, Marco Paggi

Politecnico di Torino, Department of Structural and Geotechnical Engineering, Corso Duca degli Abruzzi 24, 10129 Torino, Italy

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A B S T R A C T

Many natural and man-made materials exhibit structure over more than one length scale. In this paper, we deal with hierarchical grained composite materials that have recently been designed to achieve superior hardness and toughness as compared to their traditional counterparts. Their nested structure, where meso-grains are recursively composed of smaller and smaller micro-grains at the different scales with a fractal-like topology, is herein studied from a hierarchical perspective. Considering a top-down approach, i.e. from the largest to the smallest scale, we propose a recursive micromechanical model coupled with a generalized fractal mixture rule for the prediction of hardness and toughness of a grained material with \( n \) hierarchical levels. A relationship between hardness and toughness is also derived and the analytical predictions are compared with experimental data.

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1. Introduction

Many natural and man-made materials exhibit a structured composition over more than one length scale. Examples of such hierarchical materials include: laminated composites [1], particulate composites [2], foams [3], cellular materials [4], as well as biological materials such as the human bones [5], tendon [6], wood [7], marine gastropods [8] and the Gecko's adhesive tissues [9,10]. Understanding the effects of hierarchy in biological materials emerges as a primary concern from the research point of view, since these information can guide the synthesis of new materials with physical properties which can be tailored to specific applications [11].

From the historical point of view, an early appreciation of the influence of multiple scales, as well as the development of a hierarchical model, can be ascribed to Archard [12] in the context of Contact Mechanics of rough surfaces. In his pioneering treatment, Archard proposed to model the asperities of rough surfaces as “protuberance upon protuberance”, following the concepts of modern fractal approaches [13,14].

In the present study, we deal with hierarchical grained composite materials that have recently been designed to achieve superior hardness and toughness as compared to their traditional counterparts [4]. Their nested structure, where meso-grains or granules are recursively composed of smaller and smaller micro-grains at the different scales, is herein studied from a hierarchical perspective (see Fig. 1, where the microstructure of a two-level hierarchical material, the so-called Double Cemented WC-Co, is compared with that of the conventional grained WC-Co).

The classical micromechanics models used for determining the mechanical parameters of heterogeneous materials with only two distinct components are usually based on bottom-up approaches, in which the properties at a smaller scale are homogenized coming up to the larger scales taking into account the material morphology (see, e.g., the theories by Ponte Castañeda [15], Suquet [16] and Dormieux et al. [17] for the material strength upscaling and the models by Budiansky and O’Connell [18], Kachanov [19] and Horii and Nemat-Nasser [20] for the elastic modulus and the fracture toughness...
upscaling). Even if more sophisticated estimates of the overall tensor mechanical properties of heterogeneous solids [21] and a comparison with the most common rules of mixture have been recently proposed [22], the application of such approaches to hierarchical materials is still an open point.

In the present paper, considering a top-down approach, i.e. from the largest to the smallest scale according to the fractal-like topology of hierarchical materials, we propose a recursive micromechanical model for the prediction of hardness and toughness of a grained material with \( n \) hierarchical levels. To this aim, the generalized fractal mixture rule recently published by Carpinteri et al. [23,24] is herein adopted in order to predict the mechanical properties of each level composing the hierarchical microstructure. Finally, a relationship between hardness and toughness of hierarchical grained materials is derived, which is used to compare the analytical predictions with experimental data for a recently designed two-level hierarchical grained material [4].

2. The effect of hierarchy on hardness

To fix ideas, before considering the more general case of a \( n \)-level hierarchical material, let us consider the simplest case of a material displaying a two-level hierarchical microstructure. Describing the material using a top-down approach, i.e. from the largest to the smallest scale, the first structural level is represented by granules, or meso-grains, embedded into a homogeneous matrix (see Fig. 2).

If we consider a specimen with a characteristic size equal to \( b \), and with \( N_1 \) meso-grains having an average diameter equal to \( d_1 \), then the volumetric fraction of the meso-grains, \( \nu_1 \), is given by \( \nu_1 = N_1 f(d_1/b)^2 \), where the coefficient \( f \) is a shape factor which is equal to \( \pi/4 \) for a squared specimen with grains having a perfect rounded shape. A second level of hierarchy can be considered if we think of the meso-grains as a composite material. For instance, each meso-grain can be composed of \( N_2 \) micro-grains having diameter equal \( d_2 \) and embedded into a matrix which may differ from that occupying the first hierarchical level. Correspondingly, if micro- and meso-grains have both rounded shapes, then the volumetric fraction of the micro-grains at the second hierarchical level is given by \( \nu_2 = N_2 (d_2/d_1)^2 \).

At this point, according to a micromechanical approach [25,26], it is possible to propose a mixture rule for the prediction of hardness of this two-levels hierarchical material. Hardness of the composite can be in fact computed as an average between the properties of the constituent phases, weighted by the corresponding volumetric contents:

\[
H_{DL} = \nu_1 H_1 + (1 - \nu_1)H_m,
\]

where \( H_m \) denotes the hardness of the matrix. Similarly, the hardness of the meso-grains, \( H_1 \), can also be estimated according to a micromechanical approach on the basis of the properties of the materials composing the second level of hierarchy.

![Fig. 1. Comparison between the microstructure of a conventional grained material and its two-level hierarchical counterpart, the so-called double-cemented DC Carbide (picture adapted from [4]).](image-url)

![Fig. 2. Scheme of a two-level hierarchical material.](image-url)
In particular, analyzing the composition of the meso-grains, we readily recognize that they display the same microstructure as that of a standard grained material, where the hard phase is embedded into a softer matrix. Hence, the use of the generalized Hall–Petch relationship proposed by Carpinteri and Pugno [23] and experimentally applied to a wide range of micro- and nano-structured grained materials in [24] can be adopted for the prediction of the homogenized hardness of these composite microstructures. According to this approach, the contribution of the grains to the hardness of a two-phase composite material can be computed as follows (the reader is referred to [24] for the detailed mathematical derivation):

$$H^{(\text{grains})} = k_h v^\gamma R^{\frac{1}{3} - 1}d_2^{1 - \frac{2}{3}}$$

(2)

where $v$ is the volumetric content of the grains, $d$ is the average grains diameter and $R$ denotes the characteristic structural dimension of the specimen. The parameter $k_h$ entering Eq. (2) is a constant of proportionality, whereas $\gamma$ is a fractal exponent ranging from $2/3$ to $1$. Both these parameters can be determined from a best-fitting procedure performed on experimental data. Eq. (2) takes into account the effect of the structural dimension, $R$, on the overall mechanical behaviour, which is responsible for the well-known size-effects in quasi-brittle materials [27,28], and that it is usually not considered in the classical mixture rules.

Eq. (2) can also be used in our recursive scheme for the prediction of hardness of a hierarchical material by noting that, at the second level of hierarchy, the reference structural dimension, $R$, corresponds to the diameter of the meso-grains, $d_1$. Similarly, the volumetric fraction and the diameters of the grains, $v$ and $d$ in Eq. (2), coincide, respectively, with $v_2$ and $d_2$. As a result, we have:

$$H_2 = k_h v_2^\gamma d_2^{1 - \frac{2}{3}},$$

(3)

and the mechanical properties of the meso-grains can be computed as follows:

$$H_1 = v_2 H_2 + (1 - v_2)H_m = k_h v_2^\gamma d_2^{1 - \frac{2}{3}} + (1 - v_2)H_m$$

(4)

Introducing Eq. (4) into Eq. (1), the final expression of our proposed two-level hierarchical mixture rule is derived:

$$H^{2L} = v_2 k_h v_2^\gamma d_2^{1 - \frac{2}{3}} + (1 - v_2)H_m,$$

(5)

where $v_2 = v_1 \times v_2$ is the actual volumetric content of the hard phase.

From this equation it is possible to compare the hardness predicted for a material displaying a hierarchical microstructure over two-levels with that for a standard grained material having the same volumetric content of the hard phase, $v_1$. In that case, in fact, a typical rule of mixture would yield the following relationships:

$$H^{\text{STD}} = H_1 = v_2 H_2 + (1 - v_2)H_m = v_1 k_h v_1^\gamma d_1^{1 - \frac{2}{3}} + (1 - v_1)H_m$$

(6)

and the relative gain in hardness, $g$, for a two-levels hierarchical material as compared to its standard counterpart is given by:

$$g_H := \frac{H^{2L} - H^{\text{STD}}}{H^{\text{STD}}} = \frac{v_2 k_h v_2^\gamma d_2^{1 - \frac{2}{3}} + (1 - v_2)H_m}{v_1 k_h v_1^\gamma d_1^{1 - \frac{2}{3}} + (1 - v_1)H_m}. $$

(7)

This formula can be further simplified by neglecting the contribution of the matrix to the hardness of the grained material, which is a condition usually satisfied, since the contribution of the hard phase is largely prevailing. Thus, in this case we get:

$$g_H \cong \left( \frac{v_2}{v_1} \right)^\gamma \left( \frac{d_2}{d_1} \right)^{\frac{1}{3} - 1} - 1,$$

(8)

where the exponent $3(\gamma - 1)/2$ is negative valued for the range of variation of the parameter $\gamma$. This equation suggests that, by considering a two-level hierarchical material with the same size of the micro-grains, $d_2$, volumetric content of the reinforcement, $v_2$, and structural dimension, $b$, as those of a standard grained material, then the relative gain increases by reducing the size of the micro-grains, $d_1$, or increasing the volumetric content of the micro-grains, $v_2$.

The above-deduced equation for the prediction of hardness of a hierarchical material with two-levels of hierarchy can be generalized to the case of $n$ hierarchical levels. In this context, it has to be noticed that, from the engineering point of view, three hierarchical levels are probably enough to cover the allowed scale range of practical interest. In fact, if we imagine a specimen with reference size, $b$, equal to 5 mm and with a ratio between the diameters of the granules at two subsequent levels of hierarchy equal to $d_i/d_{i-1} = 1/100$, then the characteristic grain size of the reinforcement at the third level of hierarchy would be as small as 5 nm.

In any case, at least theoretically, a rule of mixture for the prediction of hardness of a material with $n$ hierarchical levels, $H^n$, can be derived according to the following top-down recursive scheme, which provides the value of the material properties at the $i$th level of hierarchy as a function of those of the preceding levels:

$$H^n = \sum_{i=1}^n g_H^{i-1} H^{i-1},$$

where $g_H^{i-1}$ is the relative gain at the $(i-1)$th level of hierarchy.
of the matrix at each level, Eq. (10) simplifies as follows:

\[
H_{\text{ll}} = H_0 = v_1H_1 + (1 - v_1)H_{m,0},
\]

\[
H_1 = v_2H_2 + (1 - v_2)H_{m,1},
\]

\[
\vdots
\]

\[
H_i = v_{i+1}H_{i+1} + (1 - v_{i+1})H_{m,i},
\]

\[
\vdots
\]

\[
H_{n-1} = v_nH_n + (1 - v_n)H_{m,n-1},
\]

\[
H_n = k_H v_n^2 d_n^{\gamma - 1} D_n^{1 - 1/\gamma},
\]

where, for the sake of generality, we have considered different matrix properties, \(H_{m,i}\), at each level. This equation set provides the following compact solution:

\[
H_{\text{ll}} = k_H v_1^2 d_1^{\gamma - 1} D_1^{1 - 1/\gamma} + \sum_{j=0}^{n-2} \left[ H_{m,j} \left( \frac{1}{v_{j+1}} - 1 \right) \frac{v_j}{v_{j+2} - v_j} \right] + H_{m,n-1} \left( \frac{1}{v_n} - 1 \right) v_n,
\]

where \(v_i = \prod_{k=1}^{i} v_k\) corresponds to the actual volumetric fraction of the hard phase. In the special case of constant properties of the matrix at each level, Eq. (10) simplifies as follows:

\[
H_{\text{ll}} = k_H v_1^2 d_1^{\gamma - 1} D_1^{1 - 1/\gamma} + (1 - v_1)H_{m,1},
\]

and, in close analogy with Eq. (8), the gain in hardness for a material with \(n\) hierarchical levels with respect to its standard grained counterpart is given by:

\[
g_H \approx \left( \frac{v_n}{v_1} \right)^{\gamma} \left( \frac{d_{n-1}}{b} \right)^{\gamma - 1} - 1, \quad \text{for } n \geq 2.
\]

A graphical representation of Eq. (12) is provided in Fig. 3, where the relative gain is plotted as a function of the number of hierarchical levels, \(n\), for different values of \(v_1\), in the case of \(\gamma = 0.95\) and a volumetric content of the grains in the last hierarchical level, \(v_n\), equal to 0.95.

3. The effect of hierarchy on fracture toughness

A mixture rule for the fracture toughness of a hierarchical composite material can also be proposed. According to Griffith, if the characteristic size of the defects is equal to \(l\), then the contribution of the grains to the fracture toughness can be considered as proportional to their strength multiplied by the square root of the characteristic crack length, i.e. \(K_{IC}^{\text{grains}} \propto \sigma^{\text{grains}} \sqrt{l}\) [29]. Moreover, the strength can be considered as proportional to the hardness, i.e. \(\sigma \propto H^{\gamma}\), giving \(K_{IC}^{\text{grains}} \propto H^{\gamma} H^{\gamma} \sqrt{l}\).

Clearly, when we are considering a real material microstructure, different plausible assumptions for \(l\) can be put forward. In standard composite materials, for instance, \(l\) may range from the size of the grains up to the characteristic dimension of the specimen. As a first approximation, we assume that the size of the existing defects might coincide with the diameter of the grains of the reinforcement, which is a real material heterogeneity, i.e. \(l \approx d_n\). This assumption implies the condition of perfect bonding between the granules and the matrix, such that the existing defects are confined into the highest level of hierarchy. The consistency of this assumption will be discussed in the sequel by comparing the model predictions with

![Fig. 3](image_url)
experimental data. On the basis of this assumption, the fracture toughness for a grained material with $n$ hierarchical levels can be computed according to the following top-down recursive scheme:
\[
K_{IC}^{nl} = K_{IC,0} = v_1 K_{IC,1} + (1 - v_1) K_{IC}^m,
\]
\[
K_{IC,1} = v_2 K_{IC,2} + (1 - v_2) K_{IC}^m,
\]
\[
\vdots
\]
\[
K_{IC,j} = v_{j+1} K_{IC,j+1} + (1 - v_{j+1}) K_{IC}^m,
\]
\[
K_{IC,n} = K_{IC,n} = v_n K_{IC,n+1} + (1 - v_n) K_{IC}^m,
\]
\[
K_{IC}^m = k_k \left( k_i v_i^2 d_{in}^{(1 - \gamma)} d_n^{1 - \frac{1}{2}} \right) d_2^{1 - \frac{1}{2}} = k_k k_i v_i^2 d_{in}^{(1 - \gamma)} d_n^{1 - \frac{1}{2}},
\]
where we have considered the same properties of the matrix, $K_{IC}^m$, at each level of hierarchy, and $k_k$ represents a constant of proportionality which can be suitably determined from experimental data. This equation set provides the following compact mixture rule for the material toughness:
\[
K_{IC}^{nl} = v_k k_k v_k^2 d_{in}^{(1 - \gamma)} d_n^{1 - \frac{1}{2}} + (1 - v_k) K_{IC}^m.
\]
In this case, the contribution of the matrix to the overall fracture toughness of the material is usually relevant and cannot be simplified as previously assumed for the hardness.

4. Relationship between hardness and toughness and experimental assessment of the proposed model

Considering a standard grained material, a relationship between hardness and toughness can be determined according to theoretical arguments. In particular, the contribution of the hard phase to the material hardness, $\Delta H^{STD}$, can be evaluated as follows:
\[
\Delta H^{STD} = H^m - (1 - v_1)H_m = v_k k_i v_i^2 b^{1 - \frac{1}{2}} d_2^{1 - \frac{1}{2}} = C_1 d_2^{1 - \frac{1}{2}},
\]
where $C_1 = v_k k_i v_i^2 b^{1 - \frac{1}{2}}$. Similarly, the toughness increment due to the reinforcement is given by:
\[
\Delta K^{STD} = K_{IC}^{STD} - (1 - v_1)K_{IC}^m = k_k \left( v_i k_i v_i^2 b^{1 - \frac{1}{2}} d_2^{1 - \frac{1}{2}} \right) d_2^{1 - \frac{1}{2}} = k_k C_1 d_2^{1 - \frac{1}{2}}.
\]
From Eq. (15) we can express the reinforcement grain size, $d_2$, in terms of the hardness increment and of the constant $C_1$:
\[
d_2 = \left( \frac{\Delta H^{STD}}{C_1} \right)^{\frac{2}{3}},
\]
Introducing Eq. (17) into Eq. (16), a closed-form relationship between hardness and toughness increments is established:
\[
\Delta K_{IC}^{STD} = k_k C_1 d_2^{1 - \frac{1}{2}} = k_k C_1 \left( \frac{\Delta H^{STD}}{C_1} \right)^{\frac{2}{3}} \left( \Delta H^{STD} \right)^{\frac{2}{3}},
\]
This procedure can also be repeated for a hierarchical material with $n$-levels of hierarchy, obtaining the following equations:
\[
\Delta H^{nl} = H^m - (1 - v_n)H_m = v_k k_i v_i^2 b^{1 - \frac{1}{2}} d_2^{1 - \frac{1}{2}} = C_n d_2^{1 - \frac{1}{2}},
\]
\[
\Delta K_{IC}^{nl} = K_{IC}^{nl} - (1 - v_n)K_{IC}^m = k_k \left( v_i k_i v_i^2 b^{1 - \frac{1}{2}} d_2^{1 - \frac{1}{2}} \right) d_2^{1 - \frac{1}{2}} = k_k C_n d_2^{1 - \frac{1}{2}},
\]
leading to the following relationship between hardness and toughness increments:
\[
\Delta K_{IC}^{nl} = k_k C_n d_2^{1 - \frac{1}{2}} = k_k C_n \left( \frac{\Delta H^{nl}}{C_1} \right)^{\frac{2}{3}} \left( \Delta H^{STD} \right)^{\frac{2}{3}},
\]
From this result we notice that Eqs. (18) and (20) are both power-law relationships in the $\Delta K_{IC}$ vs. $\Delta H$ plane. If we assume that the fractal exponent $\gamma$ is the same in both cases, then we recognize that the exponent of the power-law is not affected by the structural hierarchy. Moreover, since $2/3 < \gamma < 1$, this exponent is negative valued, in agreement with the well-known experimental observation that toughness is inversely related to hardness for a given material [4]. The effect of the hierarchical microstructure can be instead recognized in the values assumed by the constants $C_n$ and $C_1$. To focus on this point, let us consider the ratio between the toughness increments for a hierarchical material and for its standard grained counterpart:
\[
\frac{\Delta K_{IC}^{nl}}{\Delta K_{IC}^{STD}} = \left( \frac{C_n}{C_1} \right)^{\frac{2}{3}} \left( \frac{\Delta H^{nl}}{\Delta H^{STD}} \right)^{\frac{2}{3}},
\]
from which we recognize that the ratio $C_n/C_1$ and its exponent are both positive valued and larger than unity. Moreover, we observe that this ratio is directly related to the hardness gain, $g_H$:

\[
\frac{C_n}{C_1} = \left( \frac{v_n}{v_1} \right) \left( \frac{d_{n-1}}{d_1} \right)^{2(7-1)} = 1 + g_H.
\]

(22)

As a direct consequence of Eq. (22), it is possible to conclude that a hierarchical material is tougher than its conventional counterpart at equivalent hardness, i.e. for $\Delta H_{\text{m}} = \Delta H_{\text{STD}}$.

Conversely, it is possible to consider the ratio between the hardness increments:

\[
\frac{\Delta H_{\text{m}}}{\Delta H_{\text{STD}}} = \left( \frac{C_1}{C_n} \right)^{2(3/3-1)} \left( \frac{\Delta K_{\text{IC}}^{\text{m}}}{\Delta K_{\text{IC}}^{\text{STD}}} \right)^{2(3/3-1)} = \left( \frac{1}{1 + g_H} \right)^{2(3/3-1)} \left( \frac{\Delta K_{\text{IC}}^{\text{m}}}{\Delta K_{\text{IC}}^{\text{STD}}} \right)^{2(3/3-1)},
\]

(23)

which permits to recognize that, since the ratio $C_1/C_n$ is less than unity and its exponent is negative, a hierarchical material is harder than its conventional counterpart at equivalent toughness, i.e. for $\Delta K_{\text{IC}}^{\text{m}} = \Delta K_{\text{IC}}^{\text{STD}}$.

To provide an experimental assessment of our proposed model, we consider as a case study the Double Cemented (DC) tungsten-carbide (WC-Co), a smart material recently designed by Fang et al. [4]. This material is a novel composite made of granules of cemented carbide embedded into a cobalt matrix. This material was described as a “composite within a composite”, since the granules, containing WC particles within a cobalt binder, are bonded within a metal matrix (see Fig. 1). Actually, this is a typical example of a two-levels hierarchical material as those addressed in this study.

Experimental results have confirmed that DC WC-Co permits to achieve higher toughness than conventional WC-Co, while maintaining adequate wear resistance, which is nearly proportional to the material hardness. Considering the experimental data reported in [4], this hierarchical material is characterized by $v_1 = 0.73$ (volumetric content of granules or meso-grains), $v_2 = 0.94$ (volumetric content of the micro-grains of WC inside each meso-grain), $d_1 = 0.068$ (actual volumetric content of the reinforcement or hard phase), $d_1 = 0.068$ (average diameter of the meso-grains), and $d_2$ ranging from 1 to 6 $\mu$m (average diameter of the micro-grains). As regards the reference size of the specimen, the experimental tests were performed according to the ASTM-B406 standard which prescribes the use of $0.5 \times 0.625 \times 1.875$ cm machined rectangular bars. Hence, we assume $b = 0.5$ cm as a reference specimen size. As far as the structural parameters entering the mixture rule are concerned, we assume $\gamma = 0.95$ according to the experimental data set of standard WC-Co analyzed in [30] and computed in [23]. The toughness of cobalt is set equal to $K_{\text{IC}}^{\text{c}} = 10$ MPa m$^{1/2}$, whereas its hardness contribution, $(1 - v_2)H_m = 0.32H_m$, is neglected, since the hardness of cobalt is generally one-third of that of the reinforcement. The hardness gain becomes equal to $g_H = (v_2/v_1)^2(d_1/b)^{2(7-1)} - 1 = 0.47$, which implies that the hardness of this two-levels hierarchical WC-Co is expected to be approximately 50% higher than that of a standard grained material with the same composition. In addition, this parameter permits to determine the shift of the characteristic curve for this hierarchical material as compared to its standard counterpart in the toughness–hardness plane. Assuming hardness as proportional to wear resistance, the toughness vs. wear resistance curve for the standard material, computed on the basis of the parameters of the generalized mixture rule for WC-Co reported in [23], and that for the hierarchical material are both reported in Fig. 4 with dashed and solid lines, respectively. A substantial agreement with the experimental data taken from [4] and superimposed to the same diagram is achieved.

5. Conclusion

A new micromechanical model has been proposed for the prediction of hardness and toughness of hierarchical grained materials. Considering a top-down approach, i.e. from the largest to the smallest scale, such hierarchical mixture rules have
been formerly established for a two-level hierarchical material, and then generalized to the case of n-levels. The effect of hierarchy on hardness and toughness of these innovative materials has been investigated and the roles played by the different design parameters for the material microstructure have been elucidated. Finally, a relationship between hardness and toughness has been established, whose outcome can be very closely compared with relevant experimental data.

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