Determination of the thickness of the embedding phase in 0D nanocomposites

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Abstract

0D nanocomposites formed by small nanoparticles embedded in a second phase are very interesting systems which may show properties that are beyond the ones observed in the original constituents alone. One of the main parameters to understand the behavior of such nanocomposites is the determination of the separation between two adjacent nanoparticles, in other words, the thickness of the embedding phase. However, its experimental measurement is extremely complicated. Therefore, its evaluation is performed by an indirect approach using geometrical models. The ones typically used represent the nanoparticles by cubes or spheres.

In this paper the used geometrical models are revised, and additional geometrical models based in other parallelohedra (hexagonal prism, rhombic and elongated dodecahedron and truncated octahedron) are presented. Additionally, a hybrid model that shows a transition between the spherical and tessellated models is proposed. Finally, the different approaches are tested on a set of titanium carbide/amorphous carbon (TiC/a-C) nanocomposite films to estimate the thickness of the a-C phase and explain the observed hardness properties.

Keywords: nanocomposite, tessellation, embedding, grain, crystal, grain boundary thickness

1. Introduction:

0D nanocomposites are formed by small particles with the three dimensions in the *nano* range (contrary to e.g. 1D nanotubes or 2D nanolayers) embedded in a secondary matrix [1]. The properties of these systems are very interesting, not only because they combine properties of both mixing phases, but also because the final properties may overcome the so-called *rule of mixture*, i.e. the properties of the nanocomposite may exceed the properties of the constituents alone [2]. The properties of the nanocomposite depend not only on the composition and the particle size, but also on the distribution of these particles within the embedding matrix, i.e. the interparticle distance. For instance, superhard nanocomposites must be composed by hard small crystallites (ca. 5 nm) separated by an amorphous phase of 0.1-0.3 nm thickness [2]. A similar concept has been developed to enhance the fracture toughness of nanocomposites [3,4]. The electrical performance of nanocomposites is also dependent on that parameter [5].

However, the experimental measurement of inter-particle distance (or thickness of the embedding phase) is difficult, even by high resolution electron microscopy. Therefore, simple geometrical models have been generally used to estimate that parameter. These models assume that all the particles are identical and equally distributed. Two geometries have been used: spherical and cubic [3–7]. The first one has the disadvantage of not filling the whole space, while the second allows this possibility (so-called *tessellation*). However, both of them are necessary to explain the observed distributions. Thus, Figure 1 shows two high resolution TEM images of titanium carbide/amorphous carbon (TiC/a-C) nanocomposite coatings [8]. In the example of Figure 1b, only two crystalline TiC particles with different orientations are observed (interplanar distances of 0.22 and 0.25 nm), which are separated apart. Nevertheless, the TiC particles are rounded, which would agree with a spherical model. In contrast, in case of Figure 1a, the sample is practically fully occupied by crystalline TiC grains (the Fourier transform of the central grain indicates that the TiC is oriented along the [110] axis). Therefore, a spherical model would fail, and a cube-like model would be more suitable.

The aim of this work is to analyze more geometrical models that tessellate the space besides the cubic one, and also to present a unified hybrid model that could combine the benefits of both approaches (spherical and tessellated).

2. Experimental details

TiC/a-C nanocomposite coatings were prepared by co-sputtering of Ti and graphite targets under Ar pressure of 0.75 Pa. The power applied to each magnetron was varied to get different chemical compositions and microstructures. Further details about the film deposition are given elsewhere [8–10]. Transmission electron microscopy (TEM) and electron energy loss spectroscopy (EELS) were carried out in a Philips CM200 microscope operated at 200 kV and equipped with a parallel detection EELS spectrometer from Gatan (766–2K) [8–10]. X-ray diffraction (XRD) measurements were carried out using Cu K α radiation in a Siemens D5000 diffractometer at an incidence angle of 1°. The Scherrer equation was used to estimate the grain size from the broadening of the (220) peak.

3. Results and discussion

Figure 2 shows five polyhedra that tessellate the space (i.e. can fully occupy the volume with face-to-face contact by translation) [11]. They are, in fact, the five so-called parallelohedra, which are composed by 4-edge and/or 6-edge faces. All the edges of the parallelohedra have the same size (L), which can be considered as their characteristic length. For the sphere, the characteristic length would be the radius. Table 1 shows the volume of these parallelohedra depending on L , which can be represented in all the cases as the product of L^3 times a constant K_1 which depends on the parallelohedron. In this work, the particle size will be considered as the distance (D) between opposed faces of the parallelohedron (or the diameter in case of the sphere), which needs to be calculated as a function of L for each system. Figure 3 shows appropriate views of each prism to illustrate the different values of D in each case. In all cases, a linear relationship between L and D can be found ($D=K_2L$), where K_2 depends on the geometrical system.

The first parallelhedron (Figs. 2a and 3a) is the *cube or hexahedron*, which is composed by 6 square faces and 8 identical vertices. In this case, the edge size L equals the interface distance D . The *hexagonal prism* (Figs. 2b and 3b) is formed by 6 square faces and 2 regular hexagonal faces, with 12 identical vertices. This body is also known as ‘elongated cube’, although this name may induce confusion, because the hexagonal prism can be constructed from the cube by adding two pairs of vertices in top (and bottom) of two opposite faces (cf. Fig. 2a and 2b). As a consequence, the lateral faces are transformed from squares to hexagons. Nevertheless, to tessellate the space, the hexagons need to be regular, which obligates to increase the distance between the square faces of the original cube. As a consequence, this body has two different inter-face distances; between the hexagonal faces (D_{hex}), the distance is the same than in the cube, while between two square faces (D_{sq}), the distance is larger (cf. Fig. 3b and Table 1). The third body is the *rhombic dodecahedron* (Figs. 2c and 3c), which is composed by 12 rhombic faces with a diagonal ratio equal $2^{1/2}$ and two pairs of angles of ca. 70.5 and 109.5°. It has 14 vertices of two types, 6 of them connected to 4 faces (through the angle of 70.5°) and 8 vertices connected to 3 faces (through the angle of 109.5°). The *elongated dodecahedron* (Figs. 2d and 3d) is the result of inserting parallel additional edges on 4 of the 6 tetra-coordinated vertices. As a consequence, four rhombs are transformed in equiaxed hexagons, which conform the body together with the unmodified 8 rhombic faces. It is worth mentioning that, in this case, the hexagons are not regular, since not all the angles are the same (2 of 109.5°, as before elongation and 4 of ca. 125.25°). In this case, there are also two different inter-face distances, depending if we consider the rhombs or the hexagons (D_{rh} and D_{hex} in Table 1). The last parallelhedron is the *truncated octahedron* (Figs. 2e and 3e), which can be constructed by truncating an octahedron or a cube with perpendicular planes to the 3 four-fold or to the 4 three-fold symmetry axes, respectively. This body is formed by 6 squares and 8 regular hexagons, and also two different inter-face distances can be found (D_{sq} and D_{hex} in Table 1).

Table 1 summarizes the values of K_2 for all the geometrical bodies considered. In all cases, $K_2 \geq 1$, which indicates that opposed faces are more separated than

the edge of the parallelohedron, as it can be expected for this type of bodies. It can also be observed that the value of K_2 increases for more complex geometrical shapes (i.e. higher number of edges). The volume of the parallelohedra can be expressed as a function of the inter-face distances instead the edge size. All these functions have the same shape (Table 1), which is the product of D^3 times a constant K_3 which depends on the parallelohedron and the face considered. It can be seen that there are four systems with similar K_3 (approximately 0.5): the sphere, the hexagonal prism, the elongated dodecahedron, and the truncated octahedron (in these cases, when considering the separation between 4-sided faces), which indicates that they occupy a similar volume in case of same D . In addition, for bodies with hexagonal faces, K_3 is always larger when considering D_{hex} . This means that the measurement of the particle size between hexagonal faces will lead to higher volumes. In addition, the "6-face/4-face" K_3 and K_2 ratios moves towards unity when the number of edges of the parallelohedra increases, indicating that the body gets more 'spherical'.

The geometrical models are constructed by considering that particles with a certain geometrical shape are embedded in a larger cell of the same shape (see schemes in Figure 4). The difference between the large cells and the particle is filled with the embedding phase. The whole material is formed by adjustment of identical cells considering the tessellation of each parallelohedron. Therefore, the volumetric calculations can be performed by analysis of only one of these cells. It is worth mentioning that the elongated dodecahedron, hexagonal prism and truncated octahedron show two different values of the thickness of the second phase depending on the faces considered and the value of D used.

The total volume of the nanocomposite is formed by unknown volumes of particles (V_C) and embedding phase (V_A), whose addition equals unity. The fraction of particles (V_C) for a tessellated system can be calculated as (cf. Table 1):

$$V_C = \frac{K_3 D^3}{K_3 (D+t)^3} = \frac{D^3}{(D+t)^3} \quad [1]$$

which can be re-arranged to

$$1 \quad r^3 + 3r^2 + 3r - S_t = 0, \quad [2]$$

2 where r is the interparticle distance to particle size ratio:

$$3 \quad r = \frac{t}{D} \quad [3]$$

4 and S_t can be expressed as a function of the volume of the particles or the
5 embedding phase:

$$6 \quad S_t = \frac{V_A}{V_C} = \frac{1-V_C}{V_C} = \frac{V_A}{1-V_A} \quad [4]$$

7 It is worth mentioning that all the geometries that tessellate can be represented
8 with the same equation, regardless of the different shapes and values of K_3 .
9 The only difference among them is that particles of the same size D would
10 result in different volumes.

11 In a spherical system, there is a certain unoccupied volume (V_U) which cannot
12 be filled by the spheres (see Figure 4f). In a compact packaging of spheres
13 (face-centered-cubic arrangement, FCC), the spheres touch each other in the
14 diagonal of the face of a cube, as indicated in Figure 4g. This cube contains
15 $1/8^{\text{th}}$ of sphere in each corner and $1/2$ of sphere in each face, up to 4 spheres in
16 total. Thus, the maximum occupied volume by the spheres in a compact
17 packaging ($V_O = 1 - V_U$) is:

$$18 \quad V_O = \frac{\frac{4}{3}\pi L^3}{\left(\frac{4L}{\sqrt{2}}\right)^3} = \frac{\frac{4}{6}\pi D^3}{\left(\frac{2D}{\sqrt{2}}\right)^3} = \frac{\pi\sqrt{2}}{6} \approx 0.74 = 74\% \quad [5]$$

19 In a spherical model two concentric spheres are considered, the inner being the
20 particles (diameter D) and the outer considering also the embedding phase
21 (diameter $D+t$). Therefore, the volume occupied by the particles in the spherical
22 model (V_C) can be calculated by replacing D by $D+t$ in the denominator of Eq. 5,
23 as:

$$24 \quad V_C = \frac{\frac{4}{6}\pi D^3}{\left(\frac{2(D+t)}{\sqrt{2}}\right)^3} = V_O \frac{D^3}{(D+t)^3} \quad [6]$$

25 which can be re-arranged to reach

$$26 \quad r^3 + 3r^2 + 3r - S_s = 0 \quad [7]$$

and S_s can be expressed as a function of the volume of the particles or the embedding phase, considering also the volume unoccupied in a spherical model, as:

$$S_s = \frac{V_o V_A}{V_C} = \frac{V_A - V_U}{1 - V_A} \quad [8]$$

Considering the similarity of equations 2 and 7, they can be represented into one as by merging S_t and S_s (Eqs. 4 and 8) using a variable volume V_L

$$r^3 + 3r^2 + 3r - \frac{V_A - V_L}{1 - V_A} = 0, V_L = \begin{cases} 0 & \text{if tessellates} \\ V_U = \frac{\pi\sqrt{2}}{6} & \text{if spherical} \end{cases} \quad [9]$$

As indicated in Figure 1, a real system evolves from spherical to tessellation when the inter-particle distance respect particle size is reduced (i.e. r becomes smaller). A hybrid model can be defined to change between both situations, as sketched in the top part of Figure 5. Such model would include a “variation zone” from one model to the other between certain arbitrary thresholds (r_1 and r_2). Thus, if $r > r_2$, the model would be spherical, and if $r < r_1$, the model would tessellate. In the intermediate region, we propose a function that changes between the two values of V_L in Eq. 9 depending on the value of r :

$$V_L(\%) = \log \left(1 + \frac{1}{10^{V_U(\%)+10^{A+Br}}} \right), \quad A = \frac{30}{r_1 - r_2}, B = 2 - r_1 \quad [10]$$

The application of Eq. 10 is depicted in the bottom part of Figure 5 using three different pairs (r_1, r_2) , which are represented by squares and circles, respectively. In the three cases, the function changes smoothly from 0 to 26% between r_1 and r_2 . These three examples of Eq. 10 have been introduced in Eq. 9 to constitute three cases of hybrid models, and they are plotted together with the spherical and tessellated models in Figure 6. Two scales of the x axis (linear and logarithmic) have been used for clarity (cf. Figs 6a and 6b, respectively). It can be seen that the tessellated model covers the whole range of volumetric composition, while the spherical one is limited up to 74% of V_C (or 26% of V_A). The proposed hybrid models show three different transitions from the spherical model to the tessellated one to overcome that gap. Nevertheless, it can be seen that relatively low values of r (e.g. $r=0.5$, which means that the inter-particle distance is half of the particle size) is correlated with relatively high values of the

1 volume of the embedding phase (over 70%). Therefore, the hybrid models need
2 to be shifted to even lower values of r , otherwise the model would change to
3 tessellated 'too soon'. The first hybrid solution (orange line, $r_1=0.25$ and $r_2=0.5$)
4 shows a transition region between ca. 80 and 50 vol. % of embedding phase,
5 which means that composites with more than 50% of particles would be
6 governed directly by the tessellated model. In the other two hybrid models, the
7 values of r_1 and r_2 have been varied to show different possibilities of tuning the
8 transition region between models. In the case of the blue line ($r_1=0.05$ and
9 $r_2=0.4$), a much wider region is obtained (from ca. 72 to 13 vol. % of embedding
10 phase). In the final example (red curve, $r_1=0$ and $r_2=0.1$), the transition is
11 confined to low values of V_A (between ca. 44% and 0). In fact, in this latter case,
12 a 'pure' tessellated model would be only operating at 100% of V_C (see Figure
13 6b). It is worth mentioning that a hybrid model that covers the whole range
14 could be constructed by setting $r_1=0$ and a very high value of r_2 (e.g. $r_2=10$),
15 although, in practice, this would mean that the hybrid model would practically
16 coincide with the tessellated one in the whole range of V_A .

17 So far, the models are absolutely generic, since no material property has been
18 introduced. In that regard, the curves that correlate the volumetric fraction and
19 t/D (particle size to interparticle distance ratio) in Figure 6 are universal.
20 However, the volumetric fraction of the phases composing a nanocomposite is
21 not typically obtained experimentally by direct measurement. Figure 7 shows
22 the 'recipe' to apply the models to calculate the interparticle distance (i.e. the
23 thickness of the embedding phase) in a particular system. Thus, the chemical
24 composition and/or phase composition are parameters that are typically known.
25 Using the molar weight and the density of the phases, the volumetric
26 concentration can be calculated. Finally, the interparticle distance can be
27 estimated if the particle size is known.

28 Figure 8 shows the application of the different models in TiC/a-C
29 nanocomposites. The TiC is considered stoichiometric ($M=59.9$, $\rho=4.93$ g/cm³)
30 [32-1383 ICDD card, Khamrabaevite], which is embedded in a matrix of a-C
31 ($M=12$ g/mol, $\rho=2.6$ g/cc) [12]. The plot in Figure 8 is equivalent to Figure 7, but
32 now applied to the TiC/a-C system. Three different x axes are depicted: Ti
33 concentration (at. %) and TiC concentration in % mol and % vol. It is worth

1 mentioning that for Ti concentrations larger of ca. 10 at. %, the interparticle
2 distance is lower than the half of the particle size. The three hybrid models
3 connect the tessellated and spherical models at different ranges of Ti content.

4 Figure 9 shows the calculation of the a-C thickness in TiC/a-C nanocomposite
5 coatings prepared by magnetron sputtering with different Ti contents and grain
6 sizes, as explained in Section 2. In this case, the phase composition was
7 measured by EELS, and the grain size by XRD [8–10]. Figure 9a shows the
8 experimental details needed to calculate the thickness of the a-C phase using
9 the different models. It can be seen that both TiC content and TiC grain size
10 grow with the Ti content. Nevertheless, the TiC grain size is pretty constant,
11 below ca. 3 nm up to 29 at. % of Ti, and then shows a clear growth. The results
12 of the application of the models are depicted in Figure 9b. In all cases, the
13 interparticle distances calculated by the tessellated model are higher than those
14 calculated by the spherical one, as it can be expected. Nevertheless, the
15 thickness of a-C shows parallel decreasing trends up to 29 at. % of Ti, and the
16 different hybrid models presented so far (orange, blue and red lines) connect
17 the tessellated and spherical models in different compositional ranges.
18 However, from 29 at. % of Ti, the trends separate apart. This is because at
19 higher Ti concentrations not only the TiC content keeps growing, but also the
20 grain size increases (cf. Figure 9a). As a consequence, the tessellated model
21 shows an increase of the a-C thickness, while the spherical one predicts a
22 reduction, down to zero. Two of the proposed hybrid models (blue line and red
23 line) show intermediate situations. In fact, a fourth hybrid model has been also
24 presented (violet line), which was constructed with values of $r_1=0$ and $r_2=0.01$
25 (see Eqs. 9 and 10). This model is very similar to the spherical one, and only
26 changes to tessellated when the particles are very close to each other. To
27 evaluate the appropriateness of the different possibilities, we can have a look to
28 the mechanical properties observed for these films. Thus, figure 9c shows the
29 hardness of the different nanocomposites depending on the Ti content, which
30 has been often interpreted in terms of particle size and thickness of the second
31 phase [2,7]. It can be seen that inclusion of less than 5 at. % of Ti in a-C causes
32 a reduction of hardness, but this effect is interpreted in terms of a lower sp^3
33 content in the a-C phase [10]. From this point, the hardness shows an

increasing trend up to 34 at. % of Ti, where the maximum of ~28 GPa is observed. From 29 to 34 at. % of Ti the tessellated model indicates an increase of a-C thickness from 0.5 to 0.75 nm, while the spherical model shows a reduction from 0.15 nm to 0. Since in that range the hardness show a clear increase, the spherical model seems to give a more logical explanation of the experimental observations, since it would indicate TiC grains more closely packaged. Therefore, a realistic hybrid model would be closer to the spherical one, and only changes to tessellated when the spheres are almost touching each other. As a consequence, the latest hybrid model (violet line) is the best alternative among those presented to explain the overall mechanical behavior in the whole compositional range, although other values of r_2 could be also correct. The final reduction of hardness observed in the latest couple of samples is probably a consequence of the too large grain size (>30 nm), which is out of the optimal (<10 nm) indicated for nanocomposites. In fact, there is an inverse correlation between hardness and grain size between these two films.

4. Conclusions

The calculation of the thickness of the embedding phase in 0D nanocomposites is typically performed using geometrical models. In this work, we have described mathematically different geometrical approaches that tessellate the space (cube, hexagonal prism, rhombic dodecahedron, elongated dodecahedron and truncated octahedron), together with a spherical one. All the models that tessellate the space are equivalent, with the only particularity that they predict different particle volumes for the same particle size. A hybrid model that connects the spherical model with the tessellated ones is presented, which can be adjusted with two different constants r_1 and r_2 . All these models have been used to calculate the thickness of a-C phase in TiC/a-C nanocomposites and explain the behavior of hardness with the content of Ti. It was concluded that a hybrid model close to a spherical one is preferred, and values of $r_1=0$ and $r_2=0.01$ are proposed.

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6. References

- [1] D. Martínez-Martínez, Nanocomposite Coatings, in: Q.J. Wang, Y.-W. Chung (Eds.), *Encycl. Tribol.*, Springer US, Boston, MA, 2013: pp. 2359–2364. http://link.springer.com/10.1007/978-0-387-92897-5_710 (accessed October 2, 2016).
- [2] S. Vepřek, The search for novel, superhard materials, *J. Vac. Sci. Technol. Vac. Surf. Films.* 17 (1999) 2401. doi:10.1116/1.581977.
- [3] A. Voevodin, J. Zabinski, Load-adaptive crystalline-amorphous nanocomposites, *J. Mater. Sci.* 33 (1998) 319–327. doi:10.1023/A:1004307426887.
- [4] D. Galvan, Y.T. Pei, J.T.M. De Hosson, Influence of deposition parameters on the structure and mechanical properties of nanocomposite coatings, *Surf. Coat. Technol.* 201 (2006) 590–598. doi:10.1016/j.surfcoat.2005.12.007.
- [5] E. Lewin, O. Wilhelmsson, U. Jansson, Nanocomposite nc-TiC/a-C thin films for electrical contact applications, *J. Appl. Phys.* 100 (2006) 54303. doi:10.1063/1.2336302.
- [6] Y. Pei, D. Galvan, J.T.M. de Hosson, Nanostructure and properties of TiC/a-C:H composite coatings, *Acta Mater.* 53 (2005) 4505–4521. doi:10.1016/j.actamat.2005.05.045.
- [7] T. Zehnder, Nanostructural and mechanical properties of nanocomposite nc-TiC/a-C:H films deposited by reactive unbalanced magnetron sputtering, *J. Appl. Phys.* 95 (2004) 4327. doi:10.1063/1.1650898.
- [8] D. Martinez-Martinez, C. Lopez-Cartes, A. Justo, A. Fernandez, J. Sanchez-Lopez, A. Garcia-Luis, M. Brizuela, J. Onate, Tailored synthesis of TiC/a-C nanocomposite tribological coatings, *J. Vac. Sci. Technol. A.* 23 (2005) 1732–1736. doi:10.1116/1.210810.
- [9] D. Martinez-Martinez, J. Sanchez-Lopez, T. Rojas, A. Fernandez, P. Eaton, M. Belin, Structural and microtribological studies of Ti-C-N based nanocomposite coatings prepared by reactive sputtering, *THIN SOLID FILMS.* 472 (2005) 64–70. doi:10.1016/j.tsf.2004.06.140.
- [10] D. Martinez-Martinez, C. Lopez-Cartes, A. Fernandez, J.C. Sanchez-Lopez, Influence of the microstructure on the mechanical and tribological behavior of TiC/a-C nanocomposite coatings, *THIN SOLID FILMS.* 517 (2009) 1662–1671. doi:10.1016/j.tsf.2008.09.091.
- [11] H.S.M. Coxeter, *Regular polytopes*, 3d ed, Dover Publications, New York, 1973.
- [12] F. Alvarez, C.C. Díaz, R.M. Valladares, A.A. Valladares, Ab initio generation of amorphous carbon structures, *Diam. Relat. Mater.* 11 (2002) 1015–1018. doi:10.1016/S0925-9635(01)00648-3.

1 **6. Tables:**

2

3 Table 1: characteristics of the different geometrical bodies used for the models.

Body (# of edges)	Volume constants K_1 [$V = K_1 L^3$]	Relation of edge with inter-face distance K_2 [$D = K_2 L$]		Volume constants K_3 [$V = K_3 D^3$]
Cube (12)	1	D	1	1
Hexagonal prism (16)	$\frac{3\sqrt{3}}{2} \approx 2.60$	D_{hex}	1	$\frac{3\sqrt{3}}{2} \approx 2.60$
		D_{sq}	$\sqrt{3} \approx 1.73$	$\frac{1}{2} = 0.5$
Rhombic dodecahedron (24)	$\frac{16\sqrt{3}}{9} \approx 3.08$	D	$\frac{2\sqrt{6}}{3} \approx 1.63$	$\frac{\sqrt{2}}{2} \approx 0.71$
Elongated dodecahedron (28)	$\frac{8}{9}(3 + 2\sqrt{3}) \approx 5.75$	D_{hex}	$\frac{2\sqrt{6}}{3} \approx 1.63$	$\frac{\sqrt{2}}{4}(2 + \sqrt{3}) \approx 1.32$
		D_{rh}	$\frac{\sqrt{2}}{6}(3 + 4\sqrt{3}) \approx 2.34$	$\frac{2^4\sqrt{2}}{13^3}(47 - 2\sqrt{3}) \approx 0.45$
Truncated octahedron (36)	$8\sqrt{2} \approx 11.31$	D_{hex}	$\sqrt{6} \approx 2.45$	$\frac{4\sqrt{3}}{9} \approx 0.77$
		D_{sq}	$2\sqrt{2} \approx 2.83$	$\frac{1}{2} = 0.5$
Sphere	$\frac{4\pi}{3} \approx 5.17$	D	2	$\frac{\pi}{6} \approx 0.52$

4

5

7. Figure captions:

Figure 1. TEM images of two TiC/a-C nanocomposite films. a) rich in crystalline TiC (enclosed a FFT of the central grain). b) rich in a-C (two TiC grains are highlighted with white circles). [8]

Figure 2. Drawings of the 5 parallelohedra that tessellate. a) Cube. b) Hexagonal prism. c) Rhombic dodecahedron. d) Elongated rhombic dodecahedron. e) Truncated octahedron.

Figure 3. Distances between opposed faces (D) in the parallelohedra depicted in Figure 2. a) Cube. b) Hexagonal prism. c) Rhombic dodecahedron. d) Elongated rhombic dodecahedron. e) Truncated octahedron. All the drawings are scaled to the same edge size (L).

Figure 4. Geometrical construction of the nanocomposite models. a) Cube. b) Hexagonal prism. c) Rhombic dodecahedron. d) Elongated rhombic dodecahedron. e) Truncated octahedron. f) sphere. All these drawings are scaled to the same inter-face distance (D). g) Calculation of the unfilled volume in a spherical model.

Figure 5. Construction of a hybrid model that connects the spherical and tessellated ones when the t/D ratio decreases. Three examples of Function 10 are shown in the bottom part, with different values of r_1 (squares) and r_2 (circles): 0.25 and 0.5 (orange), 0.05 and 0.4 (blue) and 0 and 0.1 (red).

Figure 6. Volume of the embedding phase as a function of the t/D ratio for tessellated and spherical models. The results of three hybrid models constructed with the functions depicted in Figure 5 are also included. For clarity, the t/D ratio is shown as linear (a) and logarithmic (b) axes.

1

2 Figure 7. Flow diagram illustrating the application of a geometrical model for
3 calculation of the thickness of the embedding phase.

4

5 Figure 8: Application of spherical, tessellated and the three hybrid models
6 (Figure 6) on TiC/a-C nanocomposites.

7

8 Figure 9. Application geometrical models on TiC/a-C nanocomposite samples
9 [10]. a) Phase composition and grain size. b) Thickness of the a-C calculated
10 with different models: spherical, tessellated, the three hybrid models in Figure 6,
11 and an additional one with $r_1=0$ and $r_2=0.01$ (violet line). c) Hardness.

12

a

b

c

d

e

MODEL

$r < r_1$:
tessellated

$r_1 < r < r_2$:
hybrid

$r > r_2$:
spherical