Micromechanics of fracturing in nanoceramics

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An overview of key experimental data and theoretical representations on fracture processes in nanoceramics is presented. The focuses are placed on crack growth in nanoceramics and their toughening micromechanics. Conventional toughening micromechanisms are discussed which effectively operate in both microcrystalline-matrix ceramics containing nanoinclusions and nanocrystalline-matrix ceramics. Particular attention is devoted to description of special (new) toughening micromechanisms related to nanoscale deformation occurring near crack tips in nanocrystalline-matrix ceramics. In addition, a new strategy for pronounced improvement of fracture toughness of ceramic materials through fabrication of ceramic–graphene nanocomposites is considered. Toughening micromechanisms are discussed which operate in such nanocomposites containing graphene platelets and/or few-layer sheets.

1. Introduction

Nanoceramics represent ceramic materials consisting of structural units (grains/crystallites) and/or at least one phase component (say, inclusions of the second phase) with sizes in the nanometre range (less than 100 nm). Nanoceramics show excellent physical, chemical and mechanical properties that are highly desired for a wide range of technologies. For instance, nanoceramics often are specified by such outstanding mechanical characteristics as superior strength, superior hardness
and good fatigue resistance [1–4]. However, the practical use of nanoceramics is limited by both
the low fracture toughness and poor ductility/machinability that most exhibit [1–4]. In particular,
the low fracture toughness of nanoceramics (as with their conventional microcrystalline
counterparts) is viewed as the bottleneck for their wide commercial applications.

At the same time, several research groups reported on enhanced fracture toughness and/or
good ductility (or even superplasticity) of high-strength nanoceramics at comparatively low
homologous temperatures (e.g. reviews [1,2,4], book [3] and original papers [5–19]). With these
experimental data on fabrication of some special, high-strength nanoceramics with enhanced
fracture toughness and/or good ductility, one hopes to achieve dramatic progress in systematic
fabrication/synthesis of such nanoceramics in the future. In order to systematically fabricate new
nanoceramics having unique mechanical properties, the relationships between the fabrication,
structure and enhanced fracture toughness must be understood. This is, however, a formidable
challenge because it requires a detailed knowledge of many technological and structural
parameters as well as how this information is coupled to the fracture processes occurring in
nanoceramics. In the context discussed, of crucial interest is the state-of-art in micromechanics
of fracturing in nanoceramics, because this scientific discipline, first of all, is focused on the
relationships between the specific structural features of nanoceramics and the specific features
of fracturing in these materials. The main aim of this paper is to provide an overview of key
experimental data and theoretical concepts concerning fracture processes in nanoceramics. A
particular attention is devoted to discussion of both new toughening micromechanisms related
to nanoscale deformation modes in nanocrystalline-matrix ceramics and a new strategy for
improvement of fracture toughness in ceramic materials through fabrication of ceramic–graphene
nanocomposites.

2. Specific structural features of nanoceramics

Fracture processes in nanoceramics are crucially influenced by their structural features. In this
section, we briefly describe the specific structural features of nanoceramics with focuses placed on
microcrystalline-matrix ceramics containing nanoinclusions and nanocrystalline-matrix ceramics.

First, let us consider the structural features of microcrystalline-matrix ceramics containing
nanoinclusions. Typical examples of such nanoceramics are as follows [1,20]: a microcrystalline-
matrix nanocomposite consisting of microscale grains of one phase with nanoscale spherical
particles of the second phase located at grain boundaries (GBs) between microscale grains
(figure 1a); a microcrystalline-matrix nanocomposite containing spherical nanocrystallites of the
second phase, embedded into microscale grains in the matrix (figure 1b); a microcrystalline-matrix
nanocomposite containing nanoscale fibres of the second phase located at GBs and/or within
microscale grain interiors (figure 1c). In doing so, the second-phase nanoparticles (figure 1a,b)
serve as either ductile inclusions or (as with fibres; figure 1c) reinforcing structural elements. In
addition, such ceramic nanocomposites can contain three or more phases.

We now consider the structural features of single- and multi-phase nanocrystalline ceramics
that represent solids consisting of nanoscale grains (nanocrystallites of sizes \( d < 100 \text{ nm} \)) divided
by GBs. In most cases, nanocrystalline ceramics consist of approximately equiaxed grains
with a narrow grain size distribution (figure 1d,e,f). At the same time, there are other
examples of grain geometry (say, elongated grains) in nanocrystalline ceramics [16]. Single-
phase nanocrystalline ceramics are schematically presented in figure 1d. Typical multi-phase
or, in other words, composite nanocrystalline ceramics consist of either equiaxed nanoscale
grains of different phases (figure 1e) or grains (the first phase) divided by GBs with a different
chemical composition (the second phase). In addition, nanocrystalline-matrix ceramics can
contain comparatively large, second-phase inclusions (grains, fibres) embedded into the matrix
(figure 1f). These and other typical classes of nanoceramics are discussed in detail by Kuntz
et al. [1].
Figure 1. Typical structures of nanoceramics. (a) Microcrystalline-matrix ceramic nanocomposite consists of microscale grains of one phase with nanoscale particles of the second phase located at grain boundaries between microscale grains. (b) Microcrystalline-matrix ceramic nanocomposite contains spherical nanocrystallites of second phase, embedded into microscale grains. (c) Microcrystalline-matrix ceramic nanocomposite contains fibres of the second phase located at grain boundaries and within microscale grain interiors. (d) Single-phase nanocrystalline ceramic consists of approximately equiaxed nanoscale grains with an narrow grain size distribution. (e) Nanocrystalline-matrix ceramic composite consists of tentatively equiaxed nanoscale grains of different phases with a narrow grain size distribution. (f) Nanocrystalline-matrix ceramic composite contains fibres of the second phase. (Online version in colour.)

The most effective way to fabricate ceramic nanocomposites having simultaneously high strength, enhanced fracture toughness and high elastic moduli is to insert carbon nanostructures—carbon nanotubes (CNTs) or graphene nanoinclusions characterized by extremely high values of strength and Young modulus—into ceramic matrixes (e.g. reviews [21–24] and original research papers [5–7,12]). Such nanocomposites typically (but not always) contain carbon nanoinclusions at GBs (figure 2) [21–25].

It is difficult to identify the generic structural features of ceramic nanocomposites, because of their variety (figures 1 and 2). In many cases, however, grain and interphase boundaries occupy large volume fractions in nanoceramics, and thereby strongly affect the fracture processes in these materials. In the context discussed, micromechanics of fracturing in nanoceramics devote a special attention to the role of interfaces in generation and growth of cracks.

Note that nanoceramics are commonly synthesized at highly non-equilibrium conditions. As a corollary, imperfections (voids, contaminations) typically exist in nanoceramics where these imperfections tend to be located at grain and interphase boundaries as well as their triple junctions.
Thus, nanoceramics have specific structural features, depending on their design and fabrication conditions. The specific structural features of nanoceramics exert significant effects on their strength characteristics and fracture toughness (see §§3–5).

3. Fracture processes in nanoceramics: general aspects and key experimental data

In general, fracture processes involve generation, growth and coalescence of cracks/voids in a solid, resulting in its separation into two or more pieces under the action of mechanical stress. Brittle fracture occurs without apparent plastic deformation, in a dramatic way involving fast growth of a large crack and/or convergence of several cracks. The brittle behaviour significantly limits structural and other applications of materials. Ductile fracture is preceded by essential plastic deformation and typically occurs through a relatively slow nucleation, growth and coalescence of voids. The ductile behaviour of materials is highly desired for a wide range of technologies.

Nanoceramics are commonly brittle at room temperature [1–4], as with their coarse-grained counterparts. Brittle fracture dominates in ceramic materials, first of all, because lattice dislocation slip (the key deformation mechanism responsible for ductile behaviour exhibited by most metallic solids) is suppressed in ceramics at room temperature.

Fracture processes in nanoceramics are crucially influenced by grain and interphase boundaries whose amounts are very large in these materials [1–4]. So, grain and interphase boundaries serve as preferable places for nanocrack nucleation and growth, because the atomic density is low, and interatomic bonds are weak at boundaries compared with the bulk phase. Besides, the extra energy of grain and interphase boundaries contributes to the driving force for intergranular fracture with cracks propagating along boundaries and releasing the extra energy, compared with intragranular fracture with cracks propagating through grain interiors. At the same time, grain and interphase boundaries are short and curved at numerous triple junctions in nanocrystalline ceramics. Therefore, if cracks tend to nucleate and grow along such boundaries, geometry of grain and interphase boundary ensembles forces cracks to have curved geometry that hampers intergranular fracture processes.

With the aforementioned factors operating in nanoceramics, there is a competition between intergranular and intragranular fracture processes. Either one of these processes dominates or they occur in a concurrent way in nanoceramics, depending on their material and structure.
parameters as well as on the conditions of loading. So, in nanocrystalline ceramics with narrow grain size distributions, cracks tend to propagate along GBs. For instance, TiN ceramics with nanoscale grains (specified by a size of 18 nm) exhibit an intergranular fracture [4]. At the same time, in the case of nanocermics with bimodal nanostructures containing both nanoscale (with a size of around 80 nm) and microscale (with a size of around 2 µm) grains, cracks propagate along the boundaries of smaller grains and penetrate interior regions of larger grains [4].

With large amounts of grain and interphase boundaries in nanocermics, fracture processes in them are sensitive to the strength of these interfaces. In particular, the mode of crack growth depends on the strength of different boundaries in a nanoceramic specimen. For example, in Al2O3–SiC ceramic nanocomposites, the interfacial fracture energy between Al2O3 and SiC is twice that of the alumina GB fracture energy [26]. Besides, in such nanocomposites, the compressive stresses generated by SiC nanoparticles located within matrix grains may reinforce the Al2O3/Al2O3 GBs [13]. Therefore, the fracture toughness can be significantly improved, and the strong boundary may force the crack to deflect into the Al2O3 grain, thus forming the intragranular fracture mode, as was observed by Liu et al. [13].

In many cases, nanocrystalline ceramics (having typical grain sizes \(d<100\) nm) and ultrafine-grained ceramics (with \(d<500\) nm) exhibit enhancement in toughness and strength, when compared with their conventional microcrystalline counterparts (e.g. pioneering papers [21,27,28] and reviews [1,2]). In particular, values of strength for ultrafine-grained and nanocrystalline ceramics at room temperature can be two to five times higher than those of microcrystalline ceramics [1,2,21,27,28]. Such high values of strength of nanocermics are considered to occur owing to the combined effects of several factors, such as reduction in flaw sizes (close to nanoscale grain sizes in nanocrystalline structures) and structural homogenization (resulting in a partial release of residual stresses resulted from the sintering process). The role of flaw sizes is described in a first approximation by the following Griffith formula for strength \(\sigma_c(d)\) of a solid containing flaw(s) of typical length \(d\) [29]:

\[
\sigma_c(d) = k \left( \frac{\gamma E}{d} \right)^{1/2},
\]

where \(\gamma\) denotes the specific surface energy of the solid, \(E\) is the Young modulus and \(k\) is the geometrical factor. (Here, for the sake of simplicity, one considers the only normal fracture mode I, neglecting the shear fracture mode II.) The flaw size \(d\) in a nanocrystalline or ultrafine-grained ceramic solid is assumed to be close to the grain size, in which case one concludes that the strength and hardness of such solids increase with diminishing the grain size (\(\approx d\)).

Although high-strength nanocermics are commonly brittle, there are experimental data indicative of enhanced fracture toughness exhibited by several special nanocrystalline ceramics at comparatively low homologous or moderate temperatures (e.g. reviews [1,2,4], book [3] and original papers [8–13,19]). These experimental data are logically explained within the concept that (i) conventional toughening micromechanisms (that dominate in microcrystalline-matrix ceramics) operate in specific, inherent to nanostructures, ways in nanocrystalline ceramics where they effectively hamper crack growth and (ii) new, special (inherent to nanocrystallinity) toughening micromechanisms come into play in nanocrystalline ceramics [30–43]. The new toughening micromechanisms are often related to specific deformation modes that operate in nanomaterials (e.g. experimental data [13,16,44,45]), but typically are not effective enough in conventional coarse-grained polycrystalline ceramics. In particular, these specific deformation modes represent deformation by nanoscale twinning [13], grain boundary sliding [44] (which is the dominant mechanism of superplastic deformation occurring in nanocrystalline ceramics at lower temperatures [2], when compared with microcrystalline ceramics), and Coble creep controlled by grain boundary diffusion [45]. In addition, Xu et al. [16] experimentally observed concurrent superplastic deformation (having grain boundary sliding as its dominant mechanism) and grain growth resulting in formation of elongated grains. The new toughening micromechanisms and specific deformation modes operating in nanocrystalline ceramics are discussed in detail in §4.
In order to enhance mechanical properties of ceramic materials, it is very effective to exploit graphene platelets/sheets as reinforcing structural elements in ceramic-matrix nanocomposites [24,25,46–52]. This new approach is based on the unique mechanical characteristics (e.g. superior values of strength and Young modulus) of graphene as well as its geometrical features that are very suitable for use of graphene platelets/sheets as inclusions in nanocomposites. In §5, we discuss this approach with particular attention being paid to micromechanics of crack growth in ceramic–graphene nanocomposites.

4. Conventional and specific toughening micromechanisms in nanoceramics

Conventional toughening micromechanisms that operate in microcrystalline-matrix ceramics are as follows: fibre toughening, ductile-phase toughening, transformation toughening and microcrack toughening (e.g. reviews [1,2]). The fibre toughening is realized through the so-called crack-bridging and -deflection effects of second-phase fibres incorporated in a ceramic matrix. The bridging effect occurs when a crack propagates and leaves behind its tip fibres that bridge opposite crack surfaces (figure 3a). In this case, there are three behaviour types exhibited by fibres that bridge a crack wake (figure 3a). The fibres either shed load from the crack tip while remaining intact or dissipate the elastic energy when they break and pull out or debond from the ceramic matrix and pull out (figure 3a). The crack deflection effect occurs when a crack tip meets with a fibre that forces the crack to change direction of its growth (figure 3a). In doing so, the crack changes its growth direction away from the axis of highest stress to a less-efficient one (figure 3a). Both the crack-bridging and -deflection effects hinder crack growth [1,2].

The ductile-phase toughening comes into play owing to incorporation of ductile (metallic) inclusions in a microcrystalline ceramic matrix (figure 3b). Such ductile inclusions provide the following factors that hinder crack growth: blunting of crack tips when they reach ductile inclusions, stress-releasing plastic deformation of ductile particles in the process zones of growing cracks and bridging effect by ductile-phase particles [1,2] (figure 3b). The latter effect occurs when a crack propagates and leaves behind its tip a ductile-phase grain that bridges opposite crack surfaces (figure 3b). In doing so, the ductile grain can be plastically deformed, or break or debond from the ceramic matrix and pull out (figure 3b). All these processes dissipate the elastic energy in the vicinity of the crack and thereby hinder crack growth.

The transformation toughening typically occurs in ceramics containing zirconia inclusions and is associated with transformations of zirconia from the tetragonal to the monoclinic phase in vicinities of growing cracks [1,2]. These transformations are driven by external stresses concentrated near crack tips. The resultant inclusions of the zirconia monoclinic phase create internal stresses that compensate for in part the external stresses (figure 3c). Because the external stresses drive crack growth, their partial compensation (release) hampers crack growth.

The microcrack toughening occurs through formation of numerous microcracks near growing large cracks (figure 3d). Microcracks are commonly initiated by the superposition of residual thermal stresses (often generated at inclusions of the second phase; figure 3d) and the external stresses concentrated near crack tips [1,2]. The formation of microcracks dissipates the elastic energy in the vicinity of a large crack and thereby hinders its growth.

The conventional toughening micromechanisms are considered in detail in [1,2]. As noted by Kuntz et al. [1], the conventional toughening micromechanisms operate not only in microcrystalline ceramics, but also in nanocrystalline-matrix ceramics. In doing so, these micromechanisms provide moderate toughness enhancement of nanocrystalline ceramics and have some specific features owing to the nanoscale and interface effects.

We now discuss new, specific toughening micromechanisms that operate in nanocrystalline ceramics, but are not effective in conventional microcrystalline ceramics. These micromechanisms typically involve plastic deformation processes mediated by grain and interphase boundaries [30–43]. Such interfacial deformation processes are dominant in nanocrystalline ceramics, for two reasons. First, the lattice dislocation slip—the main mode of plastic flow in metals—is suppressed in both microcrystalline and nanocrystalline ceramics at ambient temperatures (owing to high
Figure 3. Conventional toughening micromechanisms in composite nanoceramics. (a) Fibre toughening is realized through the crack-bridging (A–C) and crack-deflection (D) effects of second-phase fibres incorporated in a ceramic matrix. The bridging effect occurs when the fibres either shed load from the crack tip while remaining intact (A) or dissipate the elastic energy when they break (B) or debond from the ceramic matrix and pull out (C). The crack deflection effect occurs when a crack tip meets with a fibre that forces the crack to change direction of its growth (D). (b) Ductile-phase toughening. Ductile inclusions provide blunting of crack tips when they reach ductile inclusions (A), stress-releasing plastic deformation of ductile particles in the process zones of growing cracks (B), and bridging effect by ductile-phase particles. In doing so, the ductile grain can be plastically deformed (C), or break and pull out (D) or debond from the ceramic matrix and pull out (E). (c) Transformation toughening occurs through transformations of zirconia particles from the tetragonal to the monoclinic phase in vicinities of growing cracks. (d) Microcrack toughening occurs through formation of numerous microcracks at second-phase nanoparticles in the vicinity of a growing large crack. (Online version in colour.)

Peierls barriers for lattice dislocation slip). Second, large amounts of grain and interphase boundaries are present in nanocrystalline ceramics where they can serve as effective carriers of plastic flow. In contrast, in microcrystalline ceramics, the role of interfaces in plastic deformation is limited, because amounts of grain and interphase boundaries in them are low. (Note that the lattice dislocation slip effectively operates in conventional microcrystalline ceramics at high homologous temperatures (more than 0.5\( T_m \), where \( T_m \) is the melting temperature). At the same time, owing to nanoscale and interface effects, the lattice dislocation slip is hampered or completely suppressed in nanocrystalline ceramics even at high homologous temperatures.)

With the specific peculiarities of plastic deformation in nanocrystalline ceramics, several specific toughening micromechanisms were proposed as those related to nanoscale plastic flow. Their generic features are as follows: nanoscale plastic deformation is carried by grain and interphase boundaries; and this plastic deformation results in creation of nanoscale defect
configurations whose stress fields compensate for in part the external stresses concentrated near crack tips and thereby hamper crack growth.

The specific toughening micromechanisms related to nanoscale plastic flow operate in both nanocrystalline ceramics and metals, because interfacial deformation modes dominate in both these nanocrystalline materials. The specific toughening micromechanisms include the GB sliding [30], the stress-driven migration of GBs [36,43], the nanoscale twin deformation carried by partials emitted from GBs [31], the creep deformation conducted by GB processes (Ashby–Verall creep carried by GB sliding accommodated by GB diffusion and grain rotations [32,33]), the cooperative GB sliding and migration process [36,37], stress-driven GB rotations [39,41], slow and fast nanoscale rotational deformation modes [35,38,40].

Note that the nanoscale deformation modes (GB sliding, GB diffusional creep and others) are not conventional in nanocrystalline and microcrystalline ceramics at low homologous temperatures. In most cases, however, these deformation modes effectively operate in nanocrystalline ceramics at moderate and elevated temperatures. Therefore, their consideration is relevant for understanding the mechanical behaviour of ceramics exploited at high-temperature conditions which are very interesting for a rather wide range of applications of ceramic materials (e.g. in heat engine components, thermal protection systems, high-temperature structural (load-bearing) elements in space and aviation systems, etc.).

Besides, there are computer simulations indicating that grain-boundary sliding and grain rotations significantly contribute to plastic flow of ceramics even at room temperature [53]. In the context discussed, these nanoscale deformation modes are worth being considered as those influencing crack growth in nanocrystalline materials even at low homologous temperatures.

For illustrative purposes, let us briefly consider the most effective toughening micromechanisms related to nanoscale plastic flow, namely the cooperative GB sliding and migration process [36,37]. The geometry of this process is schematically presented in figure 4. Figure 4a shows a two-dimensional section of a deformed nanocrystalline specimen containing a crack. Within the approach [36,37], GB sliding occurs under the applied shear stress and transforms the initial configuration I of GBs (figure 4b) into configuration II (figure 4c). In doing so, according to [36,37], GB sliding results in the formation of a dipole of wedge disclinations (rotational defects) A and C in configuration II (figure 4c) characterized by strengths $\pm \omega$, whose magnitude $\omega$ is equal to the tilt misorientation of the GB AB. The distance between the disclinations A and C is equal to the magnitude $x$ of the relative displacement of grains (figure 4c).

Following [36,37], in parallel with GB sliding, stress-driven GB migration often occurs as well, so that the stress fields of defects created by GB sliding are, in part, accommodated by those of the defects created by GB migration. This cooperative GB sliding and migration process transforms the initial configuration I (figure 4b) into the final configuration III (figure 4d) containing two disclination dipoles CD and BE (figure 4d).

The effect of the cooperative GB sliding and migration on the fracture toughness of nanocrystalline solids was calculated and analysed in the exemplary case of nanocrystalline 3C–SiC (the cubic phase of silicon carbide) specified by the grain size $d = 15$ nm [37]. The effect in question is characterized by the ratio $K_{IC}/K_{IC}^\sigma$, where $K_{IC}$ is the fracture toughness in the situation when the cooperative GB sliding and migration process occurs, and $K_{IC}^\sigma$ is the fracture toughness for brittle fracture occurring without this process. Following estimates given in [37], the ratio $K_{IC}/K_{IC}^\sigma$ at $\omega = 45^\circ$, $30^\circ$ and $15^\circ$ is equal to 1.68, 1.96 and 3.40, respectively, for a crack growing within grain interiors, and to 1.63, 1.90 and 3.65, respectively, for a crack growing along GBs. With these estimates, one concludes that the toughening micromechanism related to the cooperative GB sliding and migration process (figure 4) [37] can essentially increase the fracture toughness of nanocrystalline ceramics. At the same time, the discussed level of toughening is not sufficient for engineering applications of ceramic materials. In particular, significantly larger values of fracture toughness (close to those of metals) are desired for exploitation of ceramics in medical implants. In this context, further research searching for new nanoceramics with enhanced toughness is highly desirable.
Figure 4. Cooperative grain boundary sliding and migration process in nanocrystalline ceramic specimen near a crack tip. 
(a) General view. (b) Initial configuration I of grain boundaries. (c) Configuration II results from grain boundary sliding. Dipole of disclinations AC is generated owing to grain boundary sliding. (d) Configuration III results from cooperative grain boundary sliding and migration process. Two disclination dipoles CD and BE are generated due to this cooperative process. (Online version in colour.)

Besides, Ovid’ko et al. [37] have calculated dependences $K_{IC}/K_{IC}^\sigma$ on grain size $d$, for nanocrystalline ceramic 3C–SiC. In particular, in the case of the disclination strength of $\omega = 30^\circ$, an increase in grain size from 10 to 100 nm leads to a decrease of the ratio $K_{IC}/K_{IC}^\sigma$ from 1.99 to 1.64. With this trend, one concludes that the cooperative GB sliding and migration process is most effective in fracture toughness enhancement in nanocrystalline ceramics with finest grains.

To summarize, conventional toughening micromechanisms (fibre toughening, ductile-phase toughening, transformation toughening, and microcrack toughening) effectively operate in microcrystalline-matrix ceramics (figure 3). Along with these conventional micromechanisms, specific toughening micromechanisms (associated with nanoscale plastic deformation) come into play in nanocrystalline ceramics and can increase their fracture toughness via a decrease of local stresses near crack tips. The micromechanisms associated with GB deformation modes are expected to be effective in fracture toughness enhancement in nanocrystalline ceramics.

Also, note that the defect configurations associated with both nanoscale deformation modes and corresponding toughening mechanisms are stable in high stresses existing near crack tips. (It is strictly demonstrated in the theoretical models discussed in this review.) However, after passage of a crack to a new position, the defect configurations stop being stable and thereby are typically destroyed. As a corollary, it is very difficult to identify these defect configurations in conventional, post-deformation experiments.

Finally, note that grain growth can occur and destroy the nanocrystalline state in nanoceramics during deformation especially at elevated temperatures. In this context, it is important that the multi-phase structures in nanocrystalline- and microcrystalline-matrix nanoceramics...
(e.g. figure 1a–c,e,f) retard grain growth and thereby contribute to the structure stability in these materials during deformation.

5. Fracture behaviour of ceramic–graphene nanocomposites

Pristine graphene—a carbon monolayer with a hexagonal covalently bonded crystal structure—is specified by highest ever measured tensile strength of $\approx 130 \text{ GPa}$ and extremely high Young modulus (in-plane stiffness) of $\approx 1.0 \text{ TPa}$ [54,55]. With these unique mechanical characteristics, graphene inclusions have a great potential to be used in improvement of strength, fracture toughness and elastic properties in ceramic-, metal- and polymer-matrix nanocomposites [24,56–58]. In particular, in order to enhance strength and fracture toughness of ceramic materials, several research groups fabricated ceramic-matrix nanocomposites containing graphene inclusions in the form of multilayer graphene or graphene oxide (GO) platelets/sheets [24,25,46–52]. Although the mechanical characteristics of these multilayer inclusions are lower than those of pristine graphene monolayer, insertion of multilayered graphene or GO platelets/sheets leads to a dramatic improvement of the fracture behaviour exhibited by ceramic–graphene nanocomposites, when compared with monolithic ceramics and other ceramic nanocomposites [24].

Note that CNTs are characterized by similar superior values of strength and elastic moduli, as with pristine graphene [21–23]. With these remarkable mechanical characteristics of CNTs, ceramic–CNTs nanocomposites show excellent mechanical properties [21–23]. More than that, in the first decade of the twenty-first century, ceramic–CNTs nanocomposites were viewed as the most promising ceramic materials for structural applications [21–23]. In recent years, however, graphene inclusions in the forms of multilayer graphene and GO platelets/sheets have been recognized as the most effective reinforcing fillers that dramatically enhance fracture toughness (and moderately improve strength) of ceramic-matrix composites [2,25,46–52]. For instance, in one experiment [46], the mechanical characteristics (Young modulus, bending strength, hardness, fracture toughness) of silicon nitride reinforced by few-layer graphene sheets showed 10–50% enhancement when compared with those of silicon nitride reinforced by CNTs. In this section, we briefly consider the mechanical properties of ceramic–graphene nanocomposites with focuses placed on toughening micromechanisms operating in these nanocomposites.

Walker et al. [47] exploited spark plasma sintering to fabricate silicon nitride–graphene nanocomposites. With homogeneously dispersed graphene sheets having thickness of 2 nm or lower ($\approx 3–4$ carbon atomic layers), the nanocomposite exhibited remarkable mechanical characteristics. In particular, a silicon nitride nanocomposite containing 1.5 vol% graphene inclusions shows $\approx 235\%$ increase in the fracture toughness (from $\approx 2.8$ to $\approx 6.6 \text{ MPa m}^{1/2}$), when compared with monolithic $\text{Si}_3\text{N}_4$ material. From a micromechanical viewpoint, toughening of the nanocomposite occurs through crack deflection, crack bridging by graphene sheets, their pull-out and necking (figure 5) [47]. It is important to note that cracks do not penetrate across graphene sheets which in fact form curved two-dimensional structures/surfaces along GBs. Instead, when a growing crack meets with a graphene sheet, it grows along the sheet and thereby follows curved path along GB surfaces. This crack deflection effectively hinders crack growth in the nanocomposites.

Tantalum carbide–graphene nanocomposites were produced by spark plasma sintering and showed high mechanical characteristics [51]. In particular, these nanocomposites exhibited 99% increase in the fracture toughness, when compared with their TaC counterparts free from graphene. The key toughening micromechanisms are experimentally revealed to be bending and kinking of graphene platelets, sliding of graphene platelets, grain wrapping by graphene, crack bridging, graphene sheet pull-out and crack deflection [51]. In addition, during the sintering process, graphene sheets are sheared off graphene platelets in TaC–graphene nanocomposites [51]. As a corollary, an averaged thickness of graphene inclusions decreases, and their aspect ratio increases. The latter geometrical factor contributes to an extra enhancement of mechanical characteristics of the nanocomposites.
To summarize, although key toughening micromechanisms in ceramic–graphene nanocomposites—crack bridging, crack deflection and crack branching—are conventional, they have the specific features responsible for remarkable enhancement in fracture toughness owing to incorporation of graphene platelets/sheets in ceramic matrixes. First of all, graphene inclusions are superstrong and have large width and length. With these characteristics, cracks typically do not penetrate graphene platelets/sheets. That is, in ceramic–graphene nanocomposites containing cracks, it is hardly possible to fracture bridging graphene inclusions. In addition, graphene platelets/sheets are bent, anchored and wrapped around ceramic grains at GBs. As a corollary, graphene inclusions have large contact area with a ceramic matrix and their geometry strongly prevents their pull-out, leading to pronounced toughening effects. Pull-out processes are accompanied by elastic straining and plastic deformation of graphene inclusions. The straining and deformation in a nanocomposite effectively dissipate its elastic energy (driving crack growth) and thereby contribute to a toughening effect.

Values of aspect ratio are very large for graphene inclusions. The geometrical factors in question contribute to an extra improvement of mechanical characteristics of the nanocomposites. In addition, during the sintering process, graphene sheets are sheared off graphene platelets in ceramic–graphene nanocomposites (in particular, in TaC–graphene nanocomposites [51]). As a corollary, an averaged thickness of graphene inclusions decreases, and their aspect ratio increases.

Finally, note that graphene inclusions are typically located at GBs, in which case they hinder grain growth during the sintering process. (For instance, the introduction of graphene nanosheets into alumina results in a reduction of grain size down to 500 nm after hot pressing, as compared to pure alumina specified by a grain size of 1000 nm after the same treatment [59].) This factor leads to comparatively small grain sizes in final ceramics and thereby contributes to their strength enhancement, compared with ceramics free from graphene.

6. Concluding remarks

In this paper, key experimental data and theoretical representations concerning both crack growth processes and toughening mechanisms/strategies in nanoceramics have been reviewed. The main conclusions are as follows. The structural features and phase content crucially affect crack growth in nanocermics. The toughening mechanisms in nanocrystalline ceramics comprise both the conventional micromechanisms (fibre toughening, ductile phase toughening, microcrack toughening and transformation toughening) typical for ceramics with various grain sizes and the mechanisms characteristic for precisely nanocrystalline ceramics. The specific toughening micromechanisms are based on nanoscale plastic flow modes specific for nanocrystalline materials and include, in particular, GB sliding, rotational deformation mode, GB rotations, GB
migration, cooperative GB sliding and migration process as well as GB diffusion. These plastic deformation modes operating near crack tips can increase the fracture toughness of nanoceramics by a factor of $\approx 1.1–3$, compared with the toughness of brittle fracture.

The newest and most effective approach to create ceramic materials with high fracture toughness is to implant graphene platelets and few-layer sheets in ceramic matrixes. Ceramic–graphene nanocomposites exhibit significantly enhanced (by a factor of $\approx 1.3–3.35$) fracture toughness owing to crack bridging, crack deflection and crack branching effects. These effects have their specific features related to extraordinarily high strength of graphene and its specific geometry (curved shape, large values of aspect ratio, large width and length of graphene platelets/sheets) in ceramic–graphene nanocomposites. Fabrication of ceramic–graphene nanocomposites for high toughness and strength is in its infancy. In the near future, one expects explosive progress in fundamental science, fabrication and applications of such nanocomposites whose potential to transform so many technologies is huge.

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References


