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Toughening of hard nanostructural thin films: a critical review

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Abstract

For engineering applications of thin films, appropriate combination of high hardness with other properties (such as high toughness, low residual stress, and good adhesion with substrate and oxidation resistance) is of vital importance. Super high hardness alone does not have too much use. For practical application, hardness and toughness are of the same importance. This paper gives a critical review on toughening methodologies for hard nanostructural thin films, these are: ductile phase toughening, nanograin boundary strengthening and sliding, composition and structure grading, multilayer design, carbon nanotube toughening, phase transformation toughening, compressive stress toughening, etc. A summary is given to cap the essence of toughening methodologies in terms of increasing the storage or dissipation of plastic energy.

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Keywords: Toughening; Hardness; Nanostructural; Thin films

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1. Introduction

Nanostructural thin films represent a new class of materials, which exhibit improved mechanical, electronic, magnetic and optical properties owing to the size effect [1–3]. Of all the exotic properties, toughness and hardness are most important for applications in manufacturing industry. Thin films with superhardness from 40 to 105 GPa have been frequently reported recently [4–8]. However, for engineering applications, film toughness is as important as, if not more than, hardness.

Toughness is the ability of a material to absorb energy during deformation up to fracture [9,10]. Fracture toughness is the ability of a material to resist the growth of a preexisting crack. According to this definition, toughness encompasses the energy required both to create the crack and to enable the crack to propagate till fracture, whereas fracture toughness only takes account of the energy required to facilitate crack propagation to fracture. These are two different concepts and should not be confused and interchangeably used.

For bulk materials and most thick films, fracture toughness is easily measured according to ASTM standards [11,12]. Under the plane strain condition, fracture toughness is related to the rate of strain energy release via [13],

$$K_c = \sqrt{\frac{EG_c}{1 - v^2}} \qquad (1)$$

Where E is the Young's modulus and v is the Poisson's ratio, G_c is the critical rate of strain energy release given by [14]:

$$G_c = \frac{\sigma_f^2 \pi a}{E} \qquad (2)$$

A plane strain condition requires that the film must be thick enough to satisfy [15]

$$h_{\min} = 2.5\left(\frac{K_{IC}}{\sigma_y}\right)^2 \qquad (3)$$

Where σ_y is the yield stress and $h_{\min}$ is the minimum thickness. For brittle materials, $(K_c/\sigma_y)^2$ is roughly 0.1 mm [16]; therefore, the minimum thickness requirement for fracture toughness measurement is 250 μm, or 0.25 mm to

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use the plane strain assumption for brittle films. Evidently, the conventional fracture toughness determination by propagating a known precrack is not suitable for thin films owing to the thickness limitation [17]. The toughness measurements for thin films seen so far can be summarized into bending or buckling, indentation and scratch tests [18–20]. In most of these testing methods, there is no known precrack to start with. The measurements thus inevitably embedded crack initiation; thus, the result is not the same as the classical "fracture toughness". It is therefore suggested [21] that, to avoid confusion, the term "toughness" be used for thin films instead of "fracture toughness".

Refs. [22–25] reviewed various toughening methodologies for bulk ceramics, or, in particular, ductile phase toughening [26,27], fiber and whisker toughening [28], transformation toughening [29], microcrack toughening [30], etc. Recently, nanosized ductile phase has also been used to toughen bulk ceramics [31,32]. However, thin films have their own virtues, thus require special methodologies to enhance their toughness. This paper summarizes the toughening designs for thin films, focusing more on nanostructured or nanocomposite thin films.

2. Ductile phase toughening

To overcome the brittleness of ceramic films, a ductile phase is often incorporated, and two mechanisms are responsible for the enhanced toughness (cf. Fig. 1): (1) Relaxation of the strain field around the crack tip through ductile phase deformation or crack blunting, whereby the work for plastic deformation is increased. (2) Bridging of cracks by ligaments of the ductile phase behind the advancing crack tip, whereby the work for plastic deformation is also increased. Musil et al. added metallic Cu [33,34], Ni [35–37] and Y [38] into nitride coatings in order to improve both hardness and toughness. Results showed that for high film toughness, crystallite size of the nitride phase should be controlled below 10 nm, and the volume of the grain boundaries greater than that of hard phase [39]. In other words, the grain boundaries must have certain thickness since too thin a grain boundary renders the toughening mechanism ineffective [40].

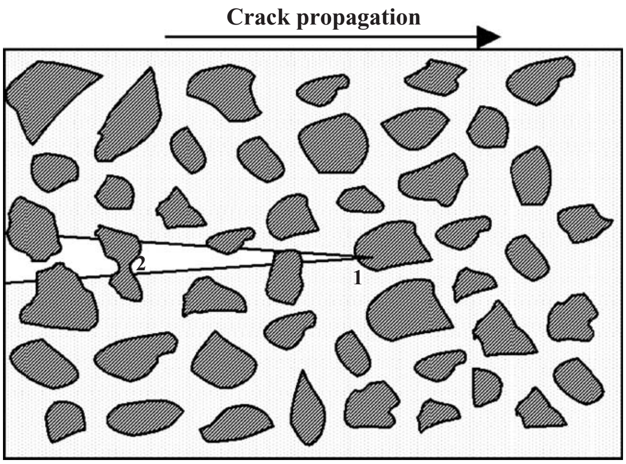

Fig. 1. Schematic diagram of ductile phase toughening through ductile phase deformation (1) crack blunting, and (2) crack bridging.

Addition of metallic phases to form Me/a-C or Me/a-C:H film (where Me is Cu, Ni or Ag) improves toughness [41–45]. The embedded metallic phase can be nanocrystalline or amorphous. In case of nanocrystalline embedment, toughening is obtained through strain release via sliding of the crystallites in the amorphous matrix [46,47]. In case of amorphous embedment, toughening is realized through relaxation of stress via plastic deformation of the amorphous phase. Zhang et al. [48] doped Al into a-C films by cosputtering of graphite and Al targets and drastically improved the film toughness. However, this came at the expense of hardness: the a-C hardness dropped from 31.5 to 8.8 GPa. In order to bring back the hardness, the authors further embedded nanocrystalline TiC into the a-C matrix doped with Al to form nc-TiC/a-C(Al) nanocomposite film and achieved a hardness of ~20 GPa while maintaining a high toughness (indentation plasticity of 55%) and very low residual stress (only 0.5 GPa).

3. Toughening through nanograin structure design

Toughness can be enhanced if crack initiation and propagation are hindered. Crack initiation needs the effective stress at the tip of an existing flaw to exceed the fracture stress of the material. The stress at the tip depends on the stress concentration factor estimated through the following equation [49]

$$\frac{\sigma_{\text{tip}}}{\sigma_{\text{applied}}} = 1 + 2\sqrt{\frac{a}{\rho}} \qquad (4)$$

Where a is length of the crack and ρ is the tip radius. Since the crack size is usually proportionally associated with grain size, the stress concentration factor can be drastically decreased by reducing grain size or flaw size to nanoscale. For example, the stress concentration factor is only 4–6 with a crack length of 1–2 nm and tip radius of 0.2–0.3 nm (one atomic bond length) in a nanostructured material, compared with that of 30–100 for the conventional bulk materials. Usually, cracks propagate along the weak region, in most cases, the grain boundaries. Therefore, hindrance of crack propagation can be realized by strengthening grain boundary and increasing boundary complicacy. As a result, in order to propagate, the crack has to undergo bending or branching, which brings about deceleration of crack propagation.

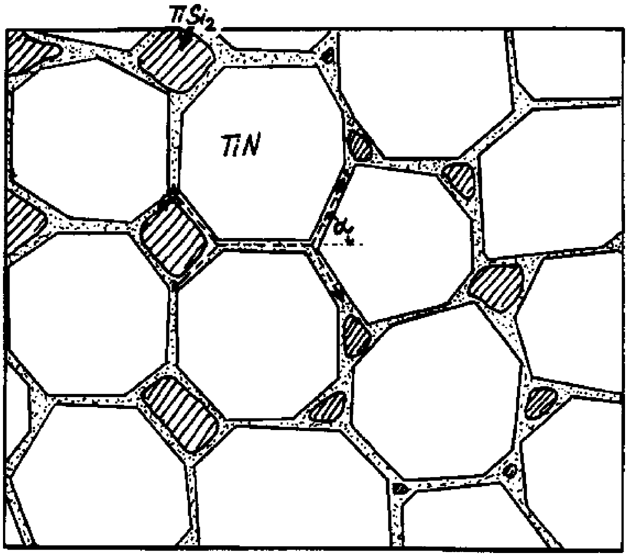

Fig. 2. Schematics of the nanostructure of nc-TiN/a-Si_3N_4/a- and nc-$TiSi_2$ nanocomposite [7].

In pursuit of films with both superior hardness and high toughness, Veprek [50–52] proposed a design concept, in which the crystallite size should be controlled to approximately 3–4 nm, and the separation between crystallites be maintained less than 1 nm to limit the flaw size. Multiphase structure should be used to maximize the interface complexity, and ternary or quaternary systems with strong tendency of segregation into binary compounds be used to form sharp and strong interfaces in order to strengthen grain boundaries. Based on this design, Veprek et al. prepared a spectrum of nanocomposite thin films by means of plasma CVD: nc-TiN/a-Si_3N_4 [53], nc-W_2N/a-Si_3N_4 [54], nc-VN/a-Si_3N_4 [55], nc-TiN/a-Si_3N_4/a- and nc-$TiSi_2$ [7], nc-TiN/a-BN [56] and nc-TiN/a-BN/a-TiB_2 [57,58]. In nc-TiN/a-Si_3N_4/a- and nc-$TiSi_2$ nanocomposite coating system, TiN nanocrystals were imbedded in an amorphous Si_3N_4 grain boundary. Amorphous $TiSi_2$ and crystallite $TiSi_2$ also exist in grain boundaries (cf. Fig. 2). An ultrahigh hardness (H_v=105 GPa [7]) was obtained in this system. The indentation test did not show microcracks, indicating a good toughness. In this design, two immiscible nitrides (nc-TiN and a-Si_3N_4) were used to achieve thermal stability [50,59], but the cohesive strength of the interface between the crystal and boundary could be degraded [60]. When local tensile stress at the crack tip is high enough, unstable crack propagation sets in [61].

Another way of enhancing film toughness is to allow certain degree of grain boundary sliding (rather than inhibiting) [62] to release the accumulated strain. Voevodin et al. [40,63] prepared nanocomposite films with carbide crystals of 10–20 nm imbedded into amorphous carbon (a-C) matrix. Crystallite size of this magnitude can restrict initial crack size and create a large volume of grain boundaries [64]. The thickness of amorphous boundary is maintained above 2 nm to prevent interaction of atomic planes in the adjacent grains and to facilitate grain boundary sliding, but less than 10 nm to restrict path of a straight crack. As a result, nc-TiC/a-C and nc-WC/a-C nanocomposite thin films achieved a “scratch toughness [65]” four- to fivefold that of the nanocrystalline carbide alone, at a slight expense of hardness.

4. Toughening through composition or structure grading

Graded interlayer is often used to reduce crack concentration and enhance adhesion between film and substrate. In gradient coating, the substrate is first covered with a highly adhesive layer, and then the coating constituents are allowed to change homogeneously or heterogeneously while the coating thickness grows to a stable outer layer [66–68]. Such a gradient design is often used in preparing thick films to enhance wear properties: a-BN films (up to 2.7 μm) deposited via a graded interlayer [69], WC-Ni film with volume fraction of WC varied gradually from top surface to substrate [70,71]. Zhang et al. [72] prepared 1.5 μm a-C gradient coating on tool steels with moderately high hardness (25 GPa) but very high toughness (plasticity of 57.6%) using magnetron sputtering by a process called bias-graded deposition. Through gradually increasing substrate bias from −20 to −150 V during deposition, graded sp^2/sp^3 fraction through the film thickness is achieved. This is not grading in composition, but grading in structure: The bottom layer has the highest sp^2/sp^3 fraction, thus the lowest residual stress and good adhesion, whereas the top layer contains the highest sp^3/sp^2 fraction to render the best tribological performance. At the same time when bias-graded coating enhances the toughness, the adhesion of the coating on tool steel shot up: with expense of about 15% in hardness, the adhesion strength increased more than two times as compared to the same coating deposited at constant bias.

5. Toughening through multilayer structure

A multilayer structure has many layers of different constituents stacking on top of one another with distinct

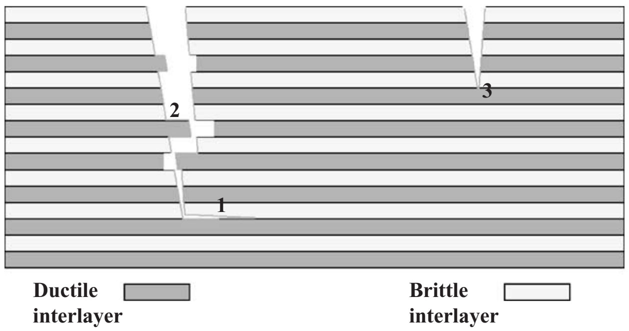

Fig. 3. Schematic representation of toughening mechanism in multilayer films: Crack deflection (1), ductile interlayer ligament bridging (2), and crack tip blunting due to nanoplasticity at interlayer (3).

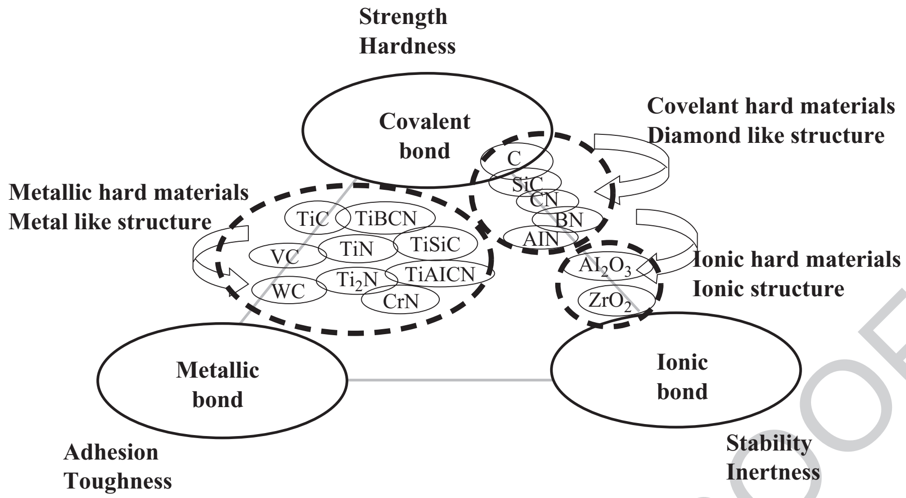

Fig. 4. Hard materials for nanocomposite coatings in the bond triangle and changes in properties with the change in chemical bonding [94].

interface between adjacent layers. Within the single layer, the composition is usually homogeneous. Multilayer structure design is another way to improve toughness of thin films, through the following three main mechanisms: crack deflection at interface between layers, ductile interlayer ligament bridging and crack tip blunting due to nanoplasticity at interface (cf. Fig. 3) [73–77]. Material selection plays an important part in this design [78]. Fig. 4 shows some potential materials that can be used for multilayer design. Covalent bonding materials have high hardness and high temperature strength; metallic bonding materials possess good adhesion and toughness; ionic bonding materials have stability and inertness. Multilayer film systems of ceramic/ceramic (such as TaN/TiN [79], ZrN/TiN [80], TiN/TiAlN [81], VN/TiAlN [82] and TiN/TiCN/TiAlN [83]), ceramic/metal (such as CrN/Cr [84], TiN/CrN/Ti [85] and TiAlN/Mo [86]) and ceramic/DLC (for example, TiC/a-C [87]) have been successfully experimented with high hardness and toughness. As an example, TiC/TiB$_2$ multilayer film composes of 100–200 single interlayer, the overall film thickness reaches about 5 μm but no cracks are found in the film with Vickers indentation up to an applied load of 100 N [88]. Multilayer film system can also be designed based on one material with different microstructures, such as a-C film with different sp^2/sp^3 ratios [89]. In multilayer film design, the number of interlayer, the thickness of each interlayer and the thickness ratio of different interlayers combine to govern the resulted toughness [90]. For instance, the fracture toughness of TiC/TiB$_2$ multilayer films decreased from 3.34 to 2.52 MPa/m$^{1/2}$ when number of total interlayers changed from 4 to 10 [91]. The fracture toughness of TiC/CrC multilayer films decreased from 4.2 to 1.4 MPa/m$^{1/2}$ while the interlayer thickness decreased from 1.2 to 0.1 μm [92]. In TiN/Ti multilayer films, the thickness of Ti layers determines the dissipation of energy, thus the degree of toughening [93].

6. Carbon nanotube toughening

Toughness of ceramic bulk materials can be improved by whisker and fiber reinforcement [95]. The toughening is obtained through crack deflection at the fiber/matrix interface, crack bridging by fiber and fiber pullout on the fracture surface (cf. Fig. 5). The same idea is applied in toughening of thin films: carbon nanotubes (CNTS) are used as “fibers” or “whiskers” to toughen nanocomposite thin films [96]. In Ref. [97], carbon nanotubes were used to enhance both hardness and toughness of alumina films. Toughness enhancement was obtained through crack deflection, cracking bridging and

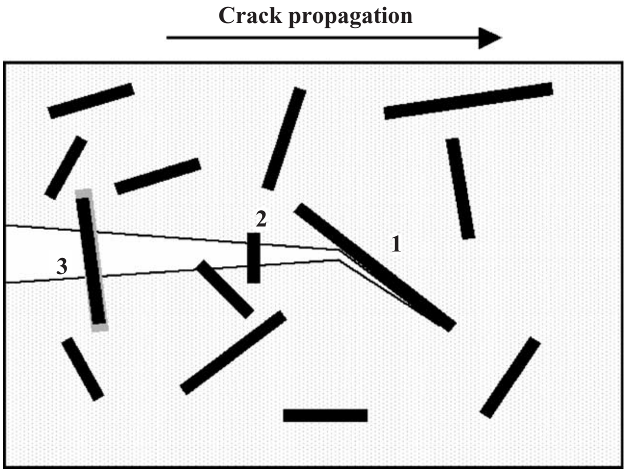

Fig. 5. Schematic diagram of fiber toughening, crack deflection (1), crack bridging (2) and fiber pullout (3).

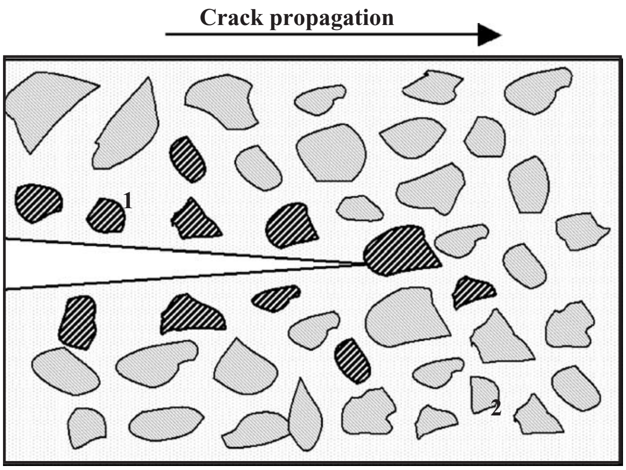

Fig. 6. Schematic diagram of transformation toughening, transformed zirconia 1 (monoclinic) and original metastable zirconia 2 (tetragonal).

fiber pullout mechanisms. Up to date, reports in this category are very scarce.

7. Phase transformation toughening

Partially stabilized zirconia (PSZ) is one of the typical examples of toughness improvement through phase transformation. Under applied stress, tetragonal zirconia phase transforms to monoclinic structure with a volume increase. This transformation occurs in the stress field around the tip of the crack, and the resultant strain involved in the transformation locally relieves the stress field and absorbs the fracture energy (cf. Fig. 6). In order to facilitate transformation toughening, retention of the high-temperature tetragonal phase is the key, and this is easily realized in film deposition. Ji et al. [98] prepared a metastable tetragonal zirconia coating by reactive D.C. magnetron sputtering, and the volume fraction of the tetragonal phase was controlled by a combination of substrate bias and postdeposition annealing. As the substrate bias was varied from 0 to −850 V, the resulting ZrO_2 crystal structure changed from random equilibrium monoclinic to random metastable tetragonal and finally strongly (111)-oriented tetragonal. Another potential candidate material for phase transformation toughening is shape memory alloy TiNi film. In TiNi films dominated by austenite structure, stress-induced martensitic transformation could help to relive the stress and increase crack propagation resistance [99].

8. Compressive stress toughening

In order to hinder crack initiation and improve toughness, compressive stress is often introduced to the surface layer of bulk materials via either ion implantation [100] or surface oxidation, which induces volume expansion [101]. This is also a common method for improvement of both hardness and toughness in thin films. Since cracking is generally initiated by tensile stresses, compressive residual stress in thin films has to be overcome first; thus, the coated component takes more tensile strain (thus, the toughness is increased [73]). Although a certain level of compressive stress increases film toughness, it should be pointed out that large residual stresses could cause delamination or cracking of the film [102]. Therefore, this method should be used with caution.

9. Summary and ending remarks

This paper reviewed the often-used toughening design and methodologies for thin films (coatings included). These methods are ductile phase toughening, grain boundary strengthening and grain boundary sliding, composition and structure grading, multilayer design, carbon nanotube toughening, phase transformation toughening and finally, and compressive stress toughening. The common basis of all the toughening methodologies is increasing of the critical failure stress (thus, cracks are difficult to form) and, once the crack forms, hindering the crack propagation. Toughening can also be achieved if the accumulated strain is properly released via dislocation propagation or grain boundary sliding; thus, crack formation is avoided.

In essence, toughening can be summarized to increasing the material's ability to absorb deformation energy, as schematically shown in Fig. 7. Toughness can be considered as the total area under the stress–strain curve ABC. It is easily seen that either raising yield stress σ_y or maximum strain ε results in larger area under the curve (thus, increasing toughness). Since hardness H is directly related

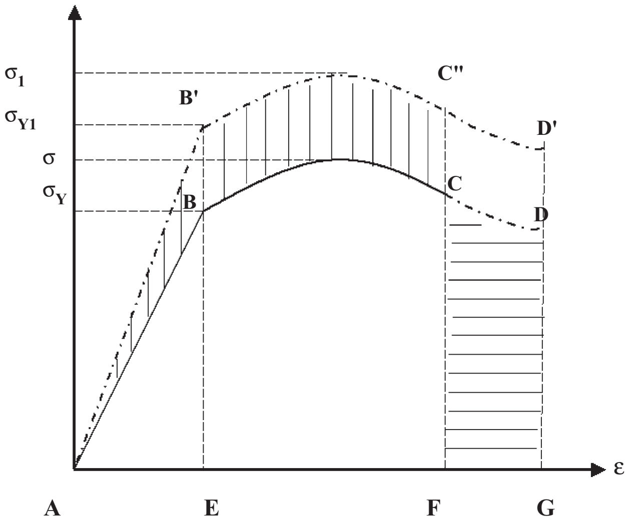

Fig. 7. Illustration of stress–strain curve obtained from tensile testing, showing starting at point A, yielding at B and fracture at C.

to σ_y through $H \approx 3\sigma_y$ [10], yield stress is increased by making the coating harder. Most hardness improvement methods for nonstructural films are thus also effective in increasing toughness (as long as the maximum strain attainable is maintained), as can be deduced from Fig. 7. Maximizing strain ε can be achieved by increasing plastic deformation (area FCDGF). Hardening plus increasing the plastic deformation result in the maximum toughness (area AB′D′GFCBA). That is the key to realization of superhard yet tough films.

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