Hard nanostructured and nanocomposite thin films

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Abstract

The article reviews the present state of the art in the field of hard nanostructured and nanocomposite films. In the first part, the origin of the enhanced hardness H of hard films is explained. Main attention is devoted to the film nanostructure and its effect on mechanical properties of hard nanocomposite films. Second part analyses the high-temperature behaviour of hard nanocomposite films and reports on a new family of hard nanocomposites with oxidation resistance exceeding 1000°C. Third part is devoted to the toughness of hard films. At the end, trends of the next development are outlined.

Keywords: Nanocomposites, Nanostructure, Hardness, Oxidation resistance, Toughness

1. Introduction

Nanostructured and nanocomposite films represent a new generation of materials. Nanocomposite films are composed of at least two separate phases with nanocrystalline and/or amorphous structure. The nanostructured and nanocomposite materials due to (i) very small (≤10 nm) grains from which they are composed and (ii) a significant role of boundary regions surrounding individual grains behave in a different manner compared to that of conventional materials with grains greater than 100 nm and so exhibit completely new properties. New unique physical and functional properties of nanostructured and nanocomposite films are a main driving force stimulating the huge development of these materials [1-11]. This article reviews the state-of-the art in the field of hard and superhard nanostructured and nanocomposite films. At present, it is accepted that the films with hardness H<40 GPa and H≥40 GPa are called the hard and superhard films, respectively.

2. Present state of knowledge

At present, it is known that (1) there are two groups of hard and superhard nanocomposites: (i) nc-MeN/hard phase and (ii) nc-MeN/soft phase, (2) nanocrystalline and/or X-ray amorphous films are created in transition regions between (i) crystalline and amorphous phases, (ii) two crystalline phases and/or (iii) two different crystallographic orientations of grains of the same material, and (3) there are huge differences in the microstructure of single- and two-phase films. Based on these findings a complete concept of the nanocomposite films with enhanced hardness was developed. This concept is based on *the geometry of nanostructured features*, i.e. the size of grains and shape of crystallites, from which the film is composed.

3. ENHANCED HARDNESS

3.1. Origin of enhanced hardness

Main mechanisms responsible for the enhanced H of hard films are: (1) dislocation-dominated plastic deformation, (2) cohesion forces between atoms, (3) nanostructure and (4) compressive macrostress σ generated in the film during its formation. The magnitude of H enhancement depends on processes operating at a given range of the size d of grains, see Fig.1. There is a critical value $d_c \approx 10$ nm at which a maximum hardness H_{max} can be achieved. A region around H_{max} corresponds to a continuous transition from the activity of *intragranular processes* at $d>d_c$, dominated by the dislocation activity and described by the Hall-Petch low ($H \sim d^{-1/2}$), to that of *intergranular processes* at $d<d_c$, dominated by a small-scale sliding in grain boundaries. The macrostress σ is undesirable and can be eliminated by a proper control of the deposition parameters.
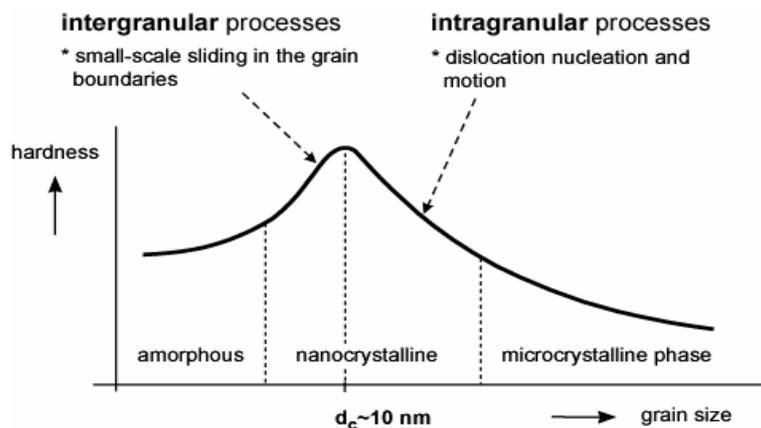

Fig.1. Schematic illustration of material hardness vs size d of grains [11].

3.2. Formation of nanostructured films

Nanocrystalline films are characterized by broad, low-intensity X-ray reflections. Such films are formed in so called transition regions where the film structure continuously or strongly changes. There are three groups of transitions: (1) transition from crystalline to amorphous phase, (2) transition between two phases of different material and (3) transition between two preferred orientations of grains of the same material, see Fig.2.
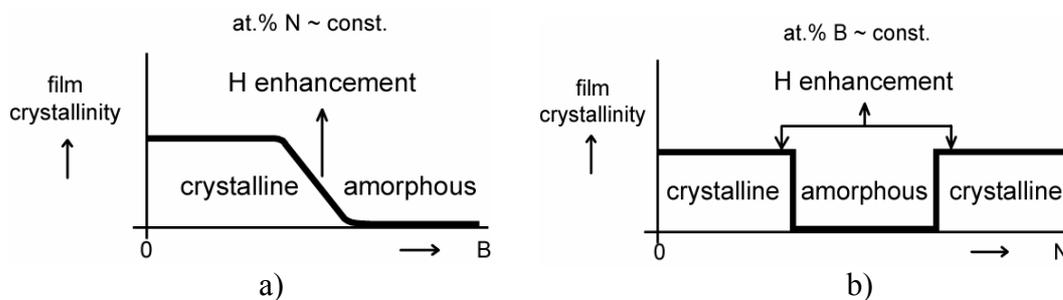

Fig.2. Schematic illustration of transition regions for $A_{1-x}B_xN$ compounds. a) Transition region from crystalline to amorphous phase and b) transition region between two crystalline phases or two preferred crystallographic orientations of grains [11].

3.3. Nanostructure of nanocomposites

Nanostructured and nanocomposite films with enhanced H can exhibit different nanostructure, see Fig.3. The films of the first group produced in a smooth transition (Fig.2a) are composed either of (i) columns (Fig.3a) or (ii) nc-grains surrounded by a thin (~1 to 2 ML) tissue phase (Fig.3b; a litlle bit higher amount of B in $A_{1-x}B_xN$ compound compared to Fig.3a). The columns are perpendicular to the substrate/film interface. The columnar nanostructure exhibit also nanocomposites of the 2nd and 3rd group produced at edges of sharp transitions (Fig.2b). On the contrary, the films nanocomposites of the 2nd and 3rd group produced between the sharp transitions are composed of a mixture of small nanograins and exhibit dense globular microstructure (Fig.3c).
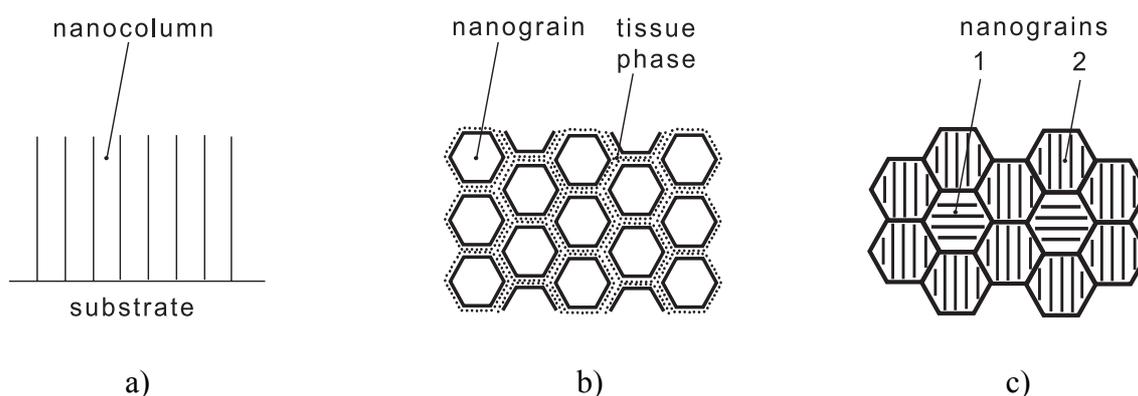

Fig.3. Schematic illustration of different nanostructures of nanocomposites with enhanced H.
a) columnar, b) nanograins surrounded by tissue phase and c) mixture of nanograins.

According to the film nanostructure, the nanostructured and nanocomposite films with enhanced H can be divided into three groups:

1. Nanocomposites with a columnar nanostructure composed of the grains assembled in nanocolumns; there is insufficient amount of the second (tissue) phase to cover the whole surface of all grains, Fig.3a.
2. Nanocomposites with a dense globular nanostructure composed of the nanograins fully surrounded by tissue phase, Fig.3b.
3. Nanocomposites with a dense globular nanostructure composed of a mixture nanograins of different materials or nanograins of different crystallographic orientations and/or lattice structures of the same material, Fig.3c.

This classification, which was confirmed experimentally, clearly shows that the origin of *enhanced H is closely connected with the size and shape of building block*s from which the nanocomposite is composed. This classification is of general validity. It means that the geometry of the grains is responsible not only for the enhanced hardness of hard nanocomposite films but also for other enhanced properties of nanostructured films, for instance, enhanced magnetic or catalytic properties.

Very important issue of this paragraph is the finding that the enhanced hardness can exhibit films which are composed of a mixture of nanograins of the same material but of different crystallographic orientations and/or different lattice structures, Fig.3c. This nanostructure explains the enhanced hardness of the *single-phase materials*. The films with columnar

nanostructure or those composed of nanograins surrounded by tissue phase are the *two-phase materials*.

4. MECHANICAL PROPERTIES OF NANOCOMPOSITE COATINGS

Mechanical properties of nanocomposite coatings are well characterized by their hardness, H, effective Young's modulus $E^*=E/(1-\nu^2)$ and elastic recovery W_e; here E is the Young's modulus and ν is the Poisson's ratio. These quantities can be evaluated from the loading/unloading curves measured by a microhardness tester. Measured values of H and E^* permit to calculate the ratio H^3/E^{*2} which is proportional to a resistance of the material to plastic deformation [12]. The likehood of plastic deformation is reduced in materials with high hardness and low modulus E^*. In general, a low modulus is desirable as it allows the given load to be distributed over a wider area. All data given in this paper were measured in our labs using a microhardness tester Fischerscope H 100 and the same methodology.

The dependencies $H=f(E^*)$, $H^3/E^{*2}=f(H)$ and $W_e=f(H)$ are basic relations between mechanical properties of thin films [5,8,13] because they determine the mechanical behaviour of thin films. For selected oxides, carbides and nitrides these dependences are displayed in Fig. 4. As can be seen from Fig.4a the dependence $H=f(E^*)$ can be approximated by a straight line

$$H[GPa]=0.15 \, E^*[GPa]-12 \qquad (1)$$

Similarly, the dependence $H^3/E^{*2}=f(H)$ given in Fig.4b can be approximated by a parabola

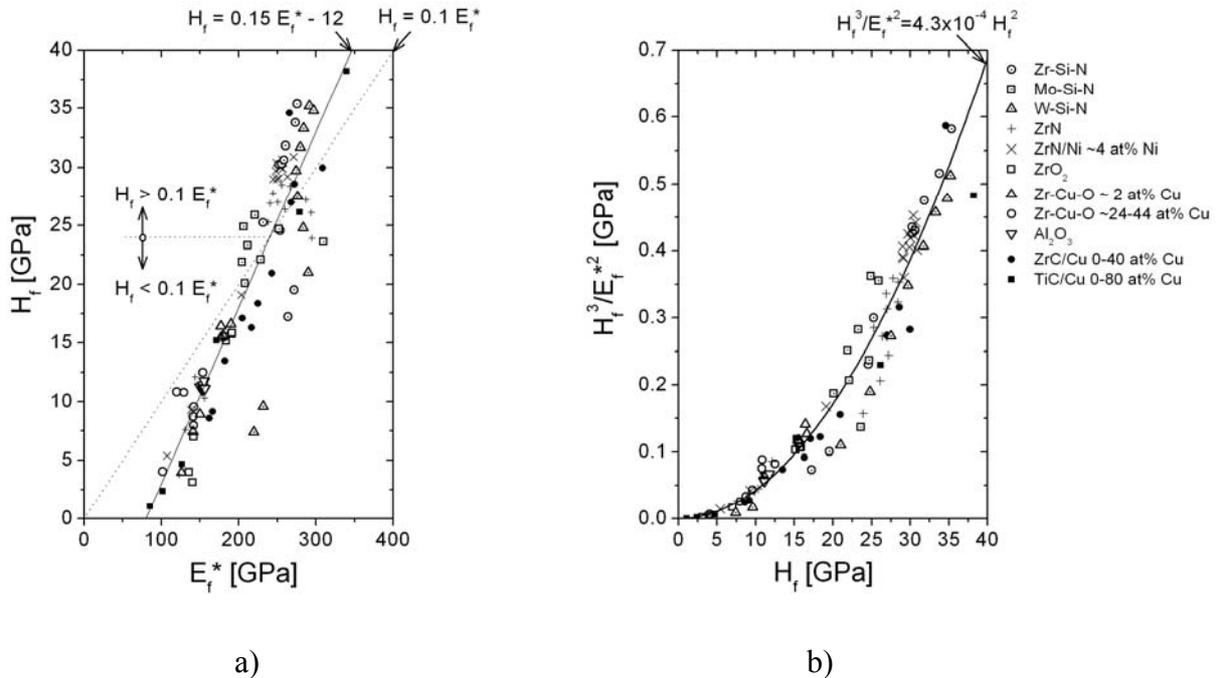$$H^3/E^{*2}=4.3 \times 10^{-3}H^2 \qquad (2)$$

Fig.4. Dependencies of (a) $H=f(E^*)$ and (b) $H^3/E^{*2}=f(H)$ for selected oxide, carbide and nitride hard films prepared by magnetron sputtering under different deposition conditions [14].

Experimental points are quite well distributed along the lines defined by Eq. (1) and (2). This finding seems to be of a fundamental importance for the prediction of mechanical behaviour

of the coating. At first, we see that in all materials displayed in Fig.4 there is a strong relation between H and E^*. H almost linearly increases with increasing E^* (Fig.4a). The scatter of experimental points around the straight line may be of different origin and needs a detailed investigation which is out of the scope of this article. At second, due to the fact that H is not exactly (1/10) E^* but $H \leq (1/10)E^*$ for $E^* \leq 240$ GPa and $H_f \geq (1/10)E_f^*$ for $E^* > 240$ GPa we can control the mechanical behaviour of the film, e.g. the resistance to plastic deformation. This fact indicates that the *general relations between H, E^* and H^3/E^{*2}* defined by Eq. (2) and (3) could be used to predict the relation between the cracking of thin film and its toughness. More details is given in [14].

In summary, it is necessary to note that the mechanical properties of the nanocomposite coating strongly depends on (i) elements which form individual phases, (ii) relative content of phases, (iii) chemical interaction between phases and (iv) its microstructure. For details see, for instance, references [5,8,13].

4. HIGH TEMPERATURE BEHAVIOUR OF HARD NANOCOMPOSITES

As was already mentioned above, unique properties of the nanocomposite films are due to their nanostructure. The nanostructure is, however, a metastable phase. This means, if the temperature under which the film is operated overpasses some threshold value T_{cr} the material of the film starts to crystallize. It results in a destruction of the nanostructure and/or the formation of new crystalline phases. This is a reason, why the nanocomposite films lose their unique properties at temperatures $T > T_{cr}$. Simply said, the temperature T_{cr}, at which the nanostructure converts into large grains and-or a new crystalline phase, determines the thermal stability of the nanocomposite. Many applications, however, require T_{cr} to be higher than 1000°C. Therefore, it is vitally important to develop new materials which will be thermally stable against crystallization and oxidation at temperatures T considerably exceeding 1000°C.

4.1. High-temperature oxidation resistance

High-temperature (high-T) oxidation resistance is very desirable property of the hard nanocomposite coatings in many applications. The oxidation resistance strongly depends on the phase composition and thermal stability of individual phases from which the coating is composed, see Fig.5.
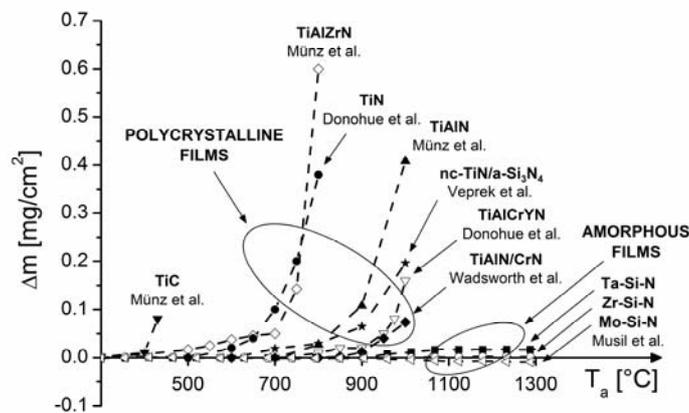

Fig.5. Oxidation resistance of selected hard binary, ternary, quaternary nitrides and hard amorphous Si_3N_4/MeN_x composite films represented as $\Delta m = f(T_a)$.

Therefore, it is not surprising that in the development of hard coatings with high-T oxidation resistance their phase composition has been varied from TiC (~400°C) through TiN (~650°C) to (Ti,Al)N (~850°C) and recently also to (Ti,Al,Y)N and Me-Si-N nanocomposites with a low (≤10 at.%) Si content (~950°C); here Me=Ti, Zr, Cr, W, Ta, Mo, Nb, etc. A common feature of all these coatings is their polycrystalline structure. These coatings are composed of grains surrounded by boundaries directly connecting the surface of the coating, exposed to an oxidation atmosphere, with the substrate. Mainly this fact is responsible for a relatively low (less than 1000°C) oxidation resistance of hard protective coatings, see Fig.5.

In principle, there is only one efficient way how to increase the oxidation resistance of hard coatings. It is based on the suppression of coating crystallization, i.e. on the elimination of grains and removing of a continuous connection between the coating surface and the substrate along the grains through boundaries surrounding them. This means that the hard coating with high-T oxidation resistance should be *amorphous*, see Fig.6. Recently, it was shown that *a new family of Si_3N_4/MeN_x composites with a high (≥50 vol.%) content of a-Si_3N_4 phase* well fulfil this requirement; a- denotes the amorphous phase [15-22]. These composite coatings are amorphous and some of them exhibit at least two unique properties (i) the excellent oxidation resistance considerably exceeding 1000°C and (ii) the high hardness ranging from 20 to 40 GPa. Unique properties of these new hard composites enable to realize new applications not mastered so far.
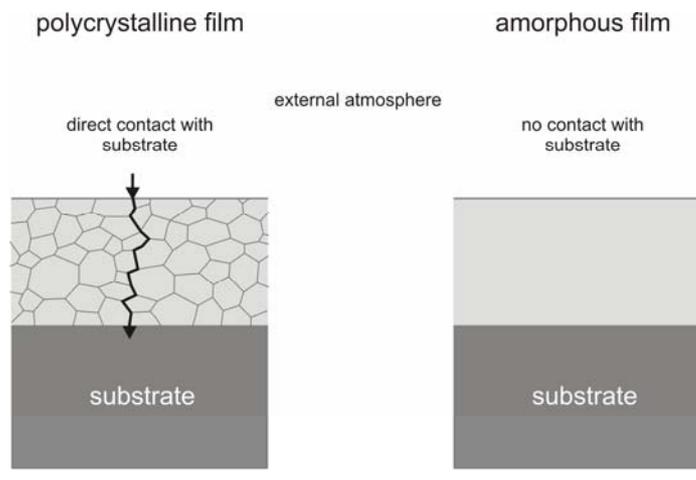

Fig.6. Schematic illustration of the contact between external atmosphere and substrate through film.

4.2. Cross-section of amorphous nanocomposites after thermal annealing

Nanocomposites with high (≥50vol.%) content of silicon nitride phase are amorphous, see Fig.7. From this figure it is seen that the bulk of Ta-Si-N film is amorphous and only the surface of film is oxidized; ~400 nm Ta_2O_5 oxide surface layer is formed. This film exhibits (i) the highest oxidation resistance, see Fig.5, and (ii) high hardness H ranging from 20 to 40 GPa. This means that theTa-Si-N film is sufficiently hard to be used in many applications, for instance, as protective coatings for cutting tools.

High amount of silicone nitride phase is not, however, a sufficient condition to reach high-T oxidation resistance. Some elements such as Mo, W, etc. form volatile oxides which are released during oxidation from the nanocomposite. This phenomenon results not only in a porous surface oxide layer, see Fig.7b, but also a lower oxidation resistance. The pores rise in consequence of the formation of the volatile MoO_x oxides outdiffusing from the surface layer of protective coating at T_a=800-1000°C. The primary cause of the decreased oxidation resistance of such protective coatings is, however, a decomposition of the metal nitride MeN_x phase in the nanocomposite. Therefore, the selection of the film elemental composition is very important in cases when a high-T oxidation resistance is required to be achieved.
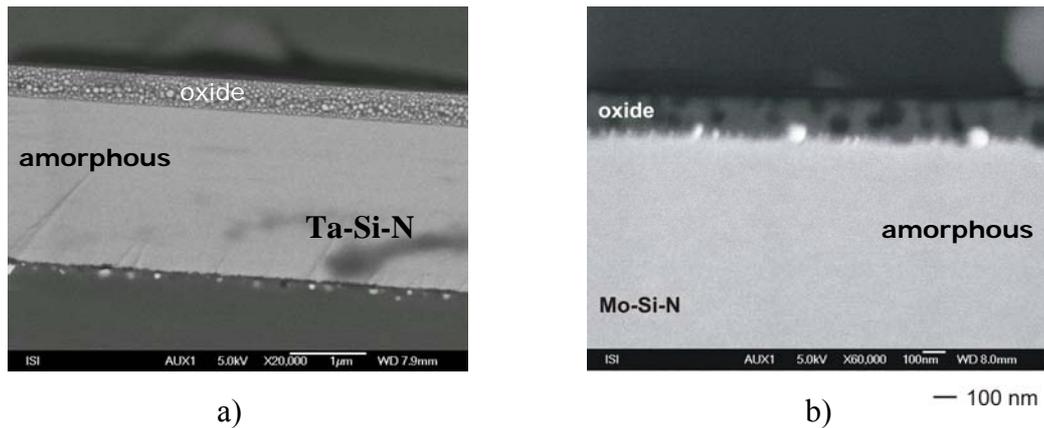

Fig.7. Cross-section of (a) Ta-Si-N film [19] and (b) Mo-Si-N film [17] on Si(100) substrate after high-T annealing in flowing air at temperature T_a=1300°C.

To achieve a good oxidation resistance at high annealing temperatures, it is necessary to ensure the highest thermal stability of both phases of the nanocomposite. The amorphous silicone nitride must be resistent against the crystallization and the metal nitride must be resistent against the decomposition ($MeN_x \rightarrow Me+N_g$). From this point of view very perspective seems to be the nanocomposites with high ($\geq$50 vol.%) of the silicon nitride, for instance, Zr-Si-N [16], Ta-Si-N [15] and Ti-Si-N phase. Nanocomposites based on oxides and oxinitrides are also very promising for the high-temperature applications.

5. TOUGHNESS OF THIN NANOCOMPOSITE COATINGS

Hardness is one of most important mechanical properties but not sufficient one to select correctly the material for a given application. The hardness must be combined with toughness because the film toughness can be for many applications more important than hardness. Therefore, it is vitaly important to master the formation of hard films with high toughness, see Fig.8.

According to the definition the toughness of material is its ability to absorb energy during deformation up to its fracture. This means that the toughness can be enhanced if cracks initiation and propagation are hindered or at least reduced. There are several ways how to reach this goal: (1) ductile phase toughening, i.e. the addition of certain ductile phases (metals) to ceramic matrices, (2) nanograin toughening based on crack deflection or branching along grain boundaries or grain boundary sliding, (3) multilayer structure toughening based on alternation of many brittle and ductile thin layers, (4) fiber or nanotubes toughening based on bridging or deflection of cracks, (5) phase transformation toughening based on the

extraction of the fracture energy and consuming it for the phase transformation and (6) compressive stress toughening which prevents the initiation of cracks by their closing.
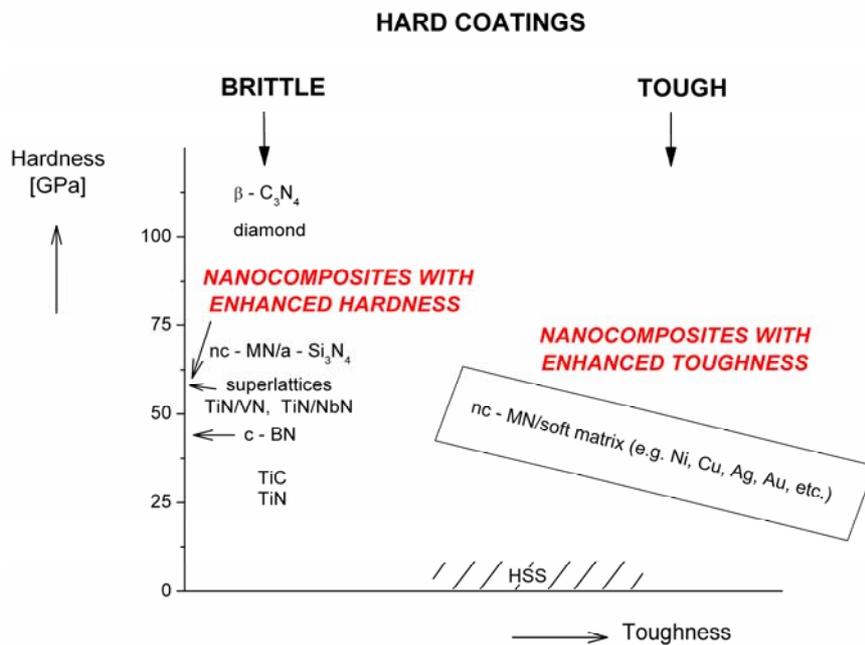
HARD COATINGS

Fig.8. Classification of nanocomposites according to their hardness and toughness.

At present, a main problem is the determination of the toughness of thin films. Recently, it was shown that the toughness of thin films can be non-destructively assessed using microindentation technique. In this assessment, the ratio H^3/E^{*2} plays an important role. The resistance of film to the formation of cracks increases with increasing ratio H_f^3/E_f^{*2}. For more details, see [11,14].

6. FUTURE TRENDS

Next activity in the field of nanostructured films will be concentrated mainly on the following problems: (1) the development of films with controlled size of grains in the range from 1 to 10 nm with the aim (a) to investigate size dependent phenomena in nanostructured films and (b) to develop new advanced coatings with unique physical and functional properties, (2) nanocrystallization from amorphous phase, (3) electronic charge transfer between nanograins with different chemical composition and different Fermi energies again with the aim to produce films with new functional properties, (4) development of new nanostructured and nanocomposite coatings based on oxides and mixture of oxides and nitrides or carbides or other compounds (5) development of protective coatings with high oxidation resistance exceeding 2000°C, (6) low temperature deposition of crystalline nanostructured functional films on heated sensitive substrates such as polymer foils and polycarbonate, and (7) development of new PVD systems for the production of nanostructured coatings under new physical conditions and with high deposition rate. Also, it can expected that very soon thin nanostructured films will serve as experimental models for the design of nanostructured bulk materials with prescribed properties.

Acknowledgements

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