

Thermal stability of nanostructured superhard coatings: A review

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Abstract

It is important to evaluate the thermal stability of hard coating because at high working temperatures the mechanical and tribological properties are deteriorated. The temperature operating on the cutting tool tip during work may reach temperatures as high as 1000 °C. Environmental considerations limiting the use of lubricants and coolant liquids, increase the necessity of finding coatings that can function at such high temperature.

Coatings can be differentiated by their hardness, H , into three main categories: hard with $H < 40$ GPa; superhard with $H > 40$ GPa; and ultra-hard coatings with $H > 80$ GPa.

There are two main reasons in the high hardness coatings: either high compressive stresses or nano-scale structure. The application of high biaxial compressive stress acts as a driving force for recovery, i.e. the higher the compressive stress, the lower is the thermal activation energy needed to initiate recovery. High biaxial compressive stress increases superhardness, but reduces the coating thermal stability. Dislocations increase the micro-scale compressive stress inside the coating and consequently, enhance recovery. In nano-scale coatings, the small nanometric scale grain size restricted grain growth and boundaries sliding, and therefore the thermal stability is enhanced.

This study treats the thermal stability of several types of superhard materials, i.e. nanocomposite coatings and those consisting of a hard transition-metal nitride and a soft metal. It focuses on formation mechanisms, materials and phase composition.

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1. Developments in stability of superhard coatings

1.1. Introduction

The development of superhard coatings, defined by hardness values above 40 GPa, has increased significantly during the last 15 years because of the interest in scientific and industrial applications. These superhard coatings possess an unusual combination of mechanical and chemical properties, such as high fracture toughness, high oxidation resistance and high thermal and chemical stability. The properties are discussed in reviews in the MRS Bulletin [1], by Barnett et al. [2,3], and in the very recently published review of Veprek et al. [4], and references therein. Levchuk and Maier [5] have recently reviewed the

influence of the preparation techniques and the deposition parameters on film hardness.

Thermal stability is a general term used to describe the change (or not) of material properties as a function of temperature. These properties include oxidation, structure, composition, mechanical properties, etc. Superhard coating exhibits high thermal stability if hardness and grain size (which depend on nanostructure and composition), measured at room temperature, remain unchanged upon annealing up to 1100 °C. Researchers have employed different methods to investigate the thermal stability of superhard coatings [4,6]: (a) measuring the hardness at room temperature after annealing at high temperatures, as studied by Herr and Broszeit [7] and by Veprek and co-workers [8–10]; (b) measuring the hardness dependence on composition (the segregation stability and diffusion between the substrate and coating), as studied by Veprek and co-workers [9,11–13] and Musil et al. [14]; (c) measuring the superlattice period L stability as a function of annealing temperature, as studied by Barnett et al. [6]; and (d) measuring the biaxial

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stresses of the coatings in the as-deposited state and the stress relaxation during the heat treatment, as studied by Mayrhofer et al. [15] and Zukerman et al. [16].

Before discussing thermal stability, it is necessary to distinguish between the various superhard coatings according to structural type, composition and hardness-enhancement mechanisms.

1.2. Classifications of superhard coatings

Superhard coatings can be classified in four separate groups: (I) intrinsically superhard materials such as diamond, diamond-like carbon (DLC), and cubic boron nitride (c-BN); (II) thin coatings in which the hardness is due to a complex, synergistic effect of ion bombardment during their deposition by plasma chemical or physical vapor deposition (PECVD or PVD); (III) nanocomposite coatings which require thermodynamically driven phase segregation; and (IV) multilayer structures.

- (I) The first group has been extensively studied and fabricated by many researchers utilizing high temperatures and high pressure as well as by utilizing PCVD and PVD techniques and are not discussed in the present study.
- (II) The second group includes thin film coatings prepared under bombardment of energetic ions during their growth and displaying hardness enhancement and nano-grain development. This ion bombardment which engenders densification and high compressive stresses, leads to improved hardness, morphology, structure and nanostructure. It has been studied and reviewed by many researchers such as Hoffman and Gaertner [17], Sundgren [18] and Bunshah [19].
- (III) The third group includes nanostructure superhard materials originating from “thermodynamically driven segregation” [4,11].
- (IV) The fourth group includes heterostructures consisting of alternating layers of transition-metal nitrides and nanocomposites consisting of transition-metal nitride nanocrystals embedded within an amorphous structure of covalent nitride [20].

Classified by nanostructure and composition, a number of superhard nanocomposite coatings systems have been reported [21–24], but four of the most studied are:

- (i) “Ti–Si–N” coatings with hardness enhancement attributed to precipitation of small Si_3N_4 particles within TiN nanocrystals [22], i.e., nc-MeN/a- Si_3N_4 , a group containing two hard phases (e.g. nc-TiN + a- Si_3N_4 , or nc-TiN/a- Si_3N_4 /a-TiSi₂);
- (ii) “Ti–B–N” coatings that are based on the immiscibility of stoichiometric TiN and TiB₂ phases [8,25];
- (iii) “super-stoichiometric TiC_{1+x} or TiC/a-C” [24,26] (similar to nc-TiN/a- Si_3N_4) [4], TiN/CN_x [27,28] and ZrN/CN_x [29]; TiC/C+MoS₂ [30];
- (iv) ncMeN/Metal (Cu, Fe, Ni, Y, Mo, Ag, Co, etc), a group containing one hard phase and a second soft phase (e.g. ncZrN+Cu) [31,32].

In the above classifications nc- and a- denote the nanocrystalline and amorphous phases respectively and MeN denotes the metal nitride (Ti, Zr, Hf, W, V, Cr, etc).

1.3. Hardness enhancement

There are different mechanisms of hardness enhancement of the coatings corresponding to their deposition and classified as groups II, III and IV.

In materials of group II, hardness enhancement occurs through energetic ion bombardment assisting in crystalline size reduction, grain boundary densification, point defects formation and increase of internal stress. Maximum hardness corresponds to maximum compressive stress and to certain PVD deposition conditions, as discussed by Musil et al. regarding TiN and TiAlVN [33,34], Herr and Broszeit [7], and reviewed by Hultman [35]. It is assumed that the defects responsible for the compressive intrinsic stresses also act as obstacles for dislocation movement thereby increasing the hardness. In fact, many studies reveal a linear correlation between stress and hardness of PVD coatings. It was reported that the highest hardness enhancement resulting from energetic ion bombardment was observed at the relatively low temperature of about 300 °C. At higher temperatures, however, hardness enhancement vanishes completely above 600–700 °C because the ion-induced effects anneal out during film growth [4]. It is the stress relaxation and lattice defect diffusion in nitrides as well as carbo-nitrides which cause the reported decrease of the apparent hardness of PVD coatings deposited at low temperatures, as reported by Oettel et al. [36], Herr and Broszeit [7], Hultman [35], and Karlsson et al. [37].

Unfortunately, the annealing of group II coatings causes defects recovery and relaxation of the ion-induced defects, reducing hardness. Therefore, if the measured hardness originated from energetic ion bombardment, the coating will lose its properties upon annealing at elevated temperatures and the structure will be thermally unstable. Musil et al. [31] were the pioneers who developed this class of nanostructured hard coatings (≥ 40 GPa) consisting of grains of transition-metal nitrides, such as ZrN or CrN, surrounded by small amounts of metal, such as copper [32] and nickel [38]. Annealing experiments to 600 °C, suggest that residual stresses, rather than the nanostructuring of the films [39], cause the enhanced hardness in these materials.

Another special class, group III, of nanocomposites was developed and described by Veprek et al. [4]. The hardness enhancement of group III superhard coating arises from nanostructural conditions, where the annealing which induces residual stress relaxation, does not affect hardness. Moreover, group III coatings possess the stable nanocomposite structure may be formed as a result of spinodal decomposition and promoted by energetic ion bombardment, but is still reliant on thermodynamic phase segregation as the driving force. They show hardness increasing at elevated temperatures of 500–600 °C, a form of “self-hardening”, as shown by Hammer et al. [40], Mitterer et al. [41], Mayrhofer et al. [42,43] and Veprek and Reiprich [11]. Group III nanostructure materials

are based on the concept of thermodynamically driven and diffusion rate-controlled (spinodal) phase segregation that leads to the formation of a stable nanostructure by self-organization [8,9,11,44]. According to Veprek et al. [4] compressive stress of 5–7 GPa alone cannot enhance the hardness of group II materials to high values, as reported by Musil and others, and the reasons for hardness enhancement, in addition to the compressive stresses, are grain size reduction, grain boundary densification and re-sputtering of weakly bonded atoms.

In materials group IV, the hardness of the multilayer structures arises from nanometer-scale of the superlattices, and the maximum hardness is achieved when the bi-layer thickness (L) is between 5 and 10 nm.

1.4. Development toward stable superhard coatings

Koehler [45] was the first to suggest producing nanometer-scale multilayer coatings with high hardness values compared to monolithic coatings. Following the approach suggested by Koehler [45], a group of researchers from Linköping University and the University of Illinois [46] reported that they succeeded to produce the nanometer-scale multilayer coatings of TiN/VN and TiN/NbN with hardness values >50 GPa. The hardness of the monolithic coating of these materials is ~20 GPa [47]. Since their breakthrough, many other nanometer-scale multilayered coatings have been investigated. In this context, Barnett and his group reported that thin film structures consisting of many alternating layers (superlattices) can exhibit high hardness when the layers repeat period is $L=2.5\text{--}5$ nm [6,46]. The thermal stability of these multilayered films depends on maintaining a distinct layer structure.

Munz and his group at Sheffield Hallam University in England [48,49] investigated the industrial applications for nanometer-scale multilayered coatings. They developed superlattice coatings consisting of TiAlCr_{0.03}N and TiAlYN with $L=1.7$ nm, TiAlN/VN and CrN/NbN with $L=3.5$ nm. This TiAlCrN/TiAlYN coating sustains its stability at 950 °C when used for high-speed cutting of die steels [49,50]. The TiAlN/VN nano-scale multilayered coating was stable only up to a temperature of 680 °C because VN converted into V₂O₅ in the presence of hot air. Regarding the CrN/NbN coating, we know that Nb exhibits high chemical stability, whereas CrN is a hard coating that can be applied with excellent adhesion at 200 °C [48]. Therefore, the combination of CrN/NbN is suitable for low-temperature applications where corrosion and wear resistance are required.

Related to nanometer-scale multilayered coatings are nanocomposite thin films with hardness approaching that of diamond. These films usually have nanocrystalline grains of transition-metal nitrides or carbides surrounded by amorphous hard nitrides. The immiscibility of the amorphous phase and nanocrystalline transition-metal nitrides is the key to developing this structure. Patscheider [51] discussed the effect of the nanostructure on coating properties, as well as the nanohardness enhancement of nanocomposite films. He mentioned that their increased hardness and lowered friction coefficients, in addition

to their thermal stability and toughness, make them interesting candidate materials for protective coatings under extreme conditions. The hardness enhancement is due to restricted dislocation movement, as it is with nanometer-scale multilayered coatings [52].

2. Stability of superhard coatings

2.1. Nanocomposite coatings

During the past decade, a new generation of coatings known as nanocomposites (nc) have been investigated. These coatings have two phases which typically consist of a primary nanocrystalline phase whose grains are encompassed by a secondary continuous matrix which may be either amorphous or nanocrystalline. It is believed that the nanocomposite by three dimensions is resembled of what was once developed for epitaxial multilayered (superlattice) coatings in one dimension. In the nanocomposite material, the small (~ nm) grain size hinders the dislocation movement, plus a possible absence of dislocations at very small grains, which increase hardness [53]. However, some deformation does occur in the composites because of grain boundary sliding. Mitterer et al. [41] and Veprek and Reiprich [11] pointed out that superhardness is the result of a well-defined interface of high cohesive strength (along with the small grain size), which prevents crack propagation along the grain boundaries. Only compounds exhibiting a certain affinity with one another, combined with a wide miscibility gap, answer these criteria and exhibit high hardness and thermal stability. For details on the relationship between nanostructure and superhardness see Refs. [4,44]. Fig. 1 (after Veprek et al. [4]) presents the thermal stability of superhard nanocomposites (nc-TiN/Si₃N₄) compared with ordinary coatings that have a hardness enhanced by energetic ion bombardment during their deposition. It can be seen that nc-TiN/Si₃N₄ prepared according to the generic design principle [11] shows high hardness and thermal stability; however, superhard coatings such as HfB₂, ZrN/Cu and ZrN/Ni fabricated by energetic ion bombardment during their deposition show low thermal stability and their hardness strongly decreases with annealing temperature.

The formation of a nanostructure with high thermal stability requires sufficiently high chemical activity of the system to provide the thermodynamic driving force for phase segregation, and a sufficiently high temperature of 500–600 °C to provide the rapid diffusion necessary to complete the segregation during growth [4].

nc-TiN/a-Si₃N₄ and nc-TiN/a-BN are two coating systems with the highest known stability at temperatures up to 1100 °C and 1000 °C, respectively. The thermal stability and self-hardening of these nanocomposites depend on the recrystallization of fine grain polycrystalline materials and on the diffusion rate at grain boundaries, i.e. immiscibility of the two phases at high temperatures [54]. It was also shown that the formation of the nc-(Al_{1-x}Ti_x)N/a-Si₃N₄ also improves oxidation resistance as compared with (Al_{1-x}Ti_x)N alone [35]. This can be explained by the formation of SiO_x in the grain

boundaries, which hinders oxygen diffusion similar to YO_x in TiAlYCrN [35].

Superlattices of nitride/boride combinations, such as TiN/TiB_2 and ZrN/ZrB ($L=7$ nm), are additional examples of nanolayers exhibiting excellent thermal stability. The hardness of the nitride/boride nanolayer coating generally remains the same or increases substantially upon annealing, but increasing the amorphous boride layer generally creates even higher hardness, explained by the crystallization of the boride layers [6].

Carvalho et al. [57] and Parreira et al. [58] deposited nanolayers of nc-MeN/a-M_2 where $\text{Me}=\text{Si, Al, Zr, W}$ and $\text{M}_2=\text{Ti, Ge}$ by magnetron sputtering, similar to those coating structures fabricated by Musil et al. (group II). The formation of the nanostructure was dependent on the ion/atom flux with hardness up to 54 GPa and elastic recovery of 74%. All structures exhibited high compressive stresses between 4 and 6 GPa. Upon annealing at 800 °C the hardness increased to ~60 GPa, but at recrystallization temperature of 900 °C the hardness decreased sharply to less than 40 GPa. High hardness with high compressive stresses was also found in Zr-Ge-N and W-Si-N systems [59–61]. The addition of Ge causes destabilization of the structure (classified as group II) and decreases in the hardness of the Zr-Ge-N system. While recrystallization in W-Si-N system after annealing at 900 °C increases the hardness, annealing at higher temperatures results in recovery, grain growth and decrease in hardness. Therefore, we can conclude that W-Si-N coatings deposited at low temperature under ion bombardment exhibit “self-hardening” upon annealing and have thermal stability up to ~800 °C. Furthermore, when oxygen was added to W-N coatings the hardness of the coating and thermal stability decreased [58].

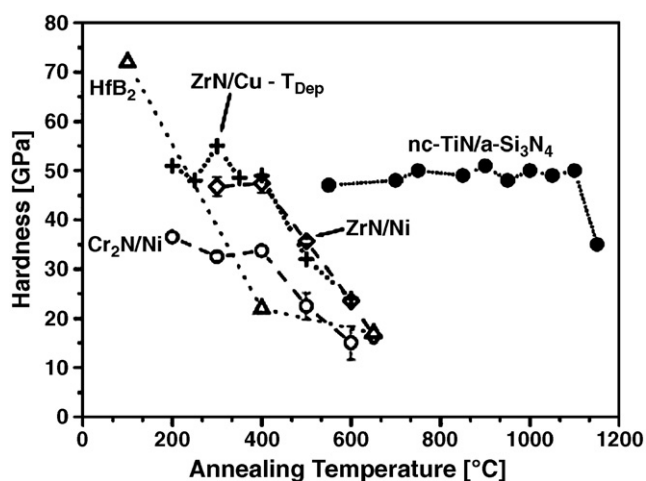


Fig. 1. (After Veprek et al. [4]) Dependence of the hardness of HfB_2 [7], $\text{Cr}_2\text{N}/\text{Ni}$, and ZrN/Ni [10] coatings hardened by energetic ion bombardment and stable superhard $\text{nc-TiN/a-Si}_3\text{N}_4$ nanocomposites on the temperature of isochronal annealing in pure nitrogen [8,9]. The hardness was measured at room temperature after each annealing step. The crosses show the dependence of the hardness of the ZrN/Cu coatings on their deposition temperature where, however, also the Cu content was slightly changing [14].

The basic technique for nanocrystalline coating production has two requirements:

- (1) co-deposition of components to form final products which are immiscible;
- (2) deposition conditions (e.g., temperature) to provide sufficient surface mobility for nano-segregation to occur and the formation of the two-phase coating. Superhard coatings should consist of hard ceramic for the nanocrystalline phase, while the other phase should form a continuum.

The superior high-temperature cutting performance of TiAlN coatings has motivated investigations studying nc-combinations of these materials [62]. Ribeiro et al. [63] deposited $\text{nc-TiAlN/a-Si}_3\text{N}_4$ using d.c. reactive magnetron sputtering; Carvalho et al. [64] deposited Ti-Al-Si-N ($\text{nc-TiN/a-Si}_3\text{N}_4$) using r.f. and d.c. reactive magnetron sputtering; Park et al. [65] deposited Ti-Al-Si-N ($\text{nc-TiN/a-Si}_3\text{N}_4$) using a sputtering and arc evaporation hybrid system; Kim et al. [66] deposited Ti-Al-Si-N ($\text{nc-TiN/a-Si}_3\text{N}_4$) coatings on WC-Co substrates using a hybrid coating system of Arc Ion Plating (AIP) and sputtering; and Veprek et al. [67] deposited $\text{nc-TiAlN/a-Si}_3\text{N}_4$ using industrial vacuum arc evaporation coating equipment. The $\text{nc-TiAlN/a-Si}_3\text{N}_4$ and $\text{nc-TiN/a-Si}_3\text{N}_4$ exhibit properties stability at temperature ≥ 900 °C.

With PVD methods, the coating structure and compounds can be modified by controlling either the bias voltage or using different substrates [64]. The various compounds are Ti-Al-Si-N solid solution, nc-TiAlN with a segregation of amorphous or nanocrystalline SiN_x and/or a segregation of amorphous AlN . These various compounds evidently control the coating's grain size and the mechanical properties. In order to ensure superhardness, the coating structure must have enough energy to enable SiN_x phase segregation. This energy can be delivered to the system by high substrate temperature or by high ion bombardment of the coating [63,64]. Carvalho et al. [64] found a maximum hardness of 54 GPa, with ~2 at.%Si in TiAlSiN , and superior thermal stability at about 900 °C, compared with ~800 °C in all other compositions [64]. Park et al. [65] related the silicon atomic percentage in the TiAlSiN to the superhardness and high elastic modulus phenomenon. The silicon solubility in the TiAlN structure is limited to about 6 at.% [65]. When it exceeds 6 at.%Si, amorphous silicon nitride starts to precipitate. It is important to note that when deposited at a relatively low temperature, silicon nitride is an amorphous phase. Park et al. [65] suggested that the amorphous phase in the $\text{TiN}/\text{Si}_3\text{N}_4$ structure hinders grain growth, thus creating a nanocomposite structure. They also found [65] that the highest hardness of 59 and highest elastic modulus of 649 GPa are achieved with 9 at.%Si. The friction coefficient decreases with the increase in silicon content, due to a formation of a self-lubricating Si(OH)_2 tribo-layer. Kim et al. [66] studied the wear rate dependence of TiAlSiN on the Si coating content and found that 9 at.%Si forms the hardest (50 GPa) and the most wear-resistant coatings at all cutting speeds. At low speeds, 19 at.%Si was found to have more wear resistance compared with 6 at.%Si, due to the formation of self-lubricating tribo-

layers such as SiO_2 or $\text{Si}(\text{OH})_2$. Park et al. and Kim et al. have followed the generic design of Veprek et al. [67] to improve the $(\text{Ti}_x\text{Al}_{1-x})\text{N}$ coating by adding Si and forming a $(\text{Ti}_x\text{Al}_{1-x})\text{N/a-Si}_3\text{N}_4$ structure. They measured a maximum hardness of ~ 50 GPa and grain size of ~ 3 nm. These properties were sustained up to 1100 °C (at least 200 °C more than the ordinary $(\text{Ti}_x\text{Al}_{1-x})\text{N}$), when the initiation of grain growth was accompanied by hardness reduction. These coatings were deposited in industrial vacuum arc coating systems [20,68] and exhibited extended cutting and drilling tool lifetimes by a factor of 2–4 over commercial TiN coating.

2.2. Superlattice coatings

For high thermal stability, the material structure should exhibit stable thermodynamic behavior (among the coating components) and form coherent low energy interfaces [69]. Most of the materials having coherent low energy interfaces are isostructural materials (e.g., Cu/Ni, TiN/NbN). Usually they are miscible, meaning that they ‘suffer’ from rapid inter-diffusion at elevated temperatures. As a result, these coatings show low thermal stability [69].

Non-isostructural nanolayers with combined metallic and compound layers, such as (ncMeN/Metal), Mo/NbN [55], W/NbN [55,56] and W/ZrN [6], exhibit excellent thermal stability and lattice match, as discussed by Barnett et al. [6]. Among the miscible superlattice structures, the TiN/NbN couple shows relatively high stability up to 700 °C [70,71]. Shinn et al. [72] published the maximum hardness values of 49 GPa for a TiN/NbN coating with a bi-layer period of $L=4.6$ nm. For $L=450$ nm the hardness reduces to 25 GPa.

Several studies have calculated superlattice stability using interlayer diffusion rate data. Engstrom et al. [73] reported that the TiN/NbN coating stability was ~ 10 h at 750 °C and 2 h at 850 °C for superlattice period of $L=4.4$ nm. Hultman et al. [70] measured a one hour lifetime at 900 °C for $L=8$ nm. Barnett and Madan [69] and Lopez et al. [71] reported that the maximum hardness of the as-deposited TiN/VN miscible superlattice coatings is 55 GPa, however, they did not study their thermal stability.

One of the most promising immiscible structures, first proposed by Barnett et al. [6], is the superlattice, BCC metal/B1-nitride system. This structure exhibits high hardness and excellent thermal stability. The group led by Barnett deposited two types of epitaxial BCC metal/B1-nitride superlattice coatings on MgO (001): Mo/NbN and W/NbN. They also deposited a polycrystalline W/ZrN superlattice on various substrates. Madan et al. [55] and Engstrom et al. [74] deposited Mo/NbN superlattice which reached a maximum hardness of 34 GPa for $L=1.4$ nm. Engstrom et al. [74] annealed the Mo/NbN superlattices at 1000 °C for 3 h and observed a transformation in the superlattice structure from Mo/NbN to MoNbN/NbN (the Mo dissolved into the NbN until it was consumed). Barnett et al. [6] also deposited a polycrystalline W/ZrN superlattice ($L=2$ – 36 nm) on various substrates. The hardness of the W/ZrN coatings was 34–39 GPa and the coating structures were stable after one hour annealing at 750 °C or 1000 °C in a non-oxidizing environment.

3. Problems and gaps

Despite of the accelerated developments in the preparation and characterization of superhard coatings during the last decade, there is still a gap between the knowledge of the preparation techniques and working parameters, and structure and thermal stability. For example, coatings with different structures and compositions may exhibit similar hardness values but different thermal stability behavior.

There are many points that need further clarification. Some of these are the following:

- (i) What is the influence of fabrication parameters, impurities contents and their composition, phase and element composition (e.g. nc-MeN/a-metal, BCC Metal/B1-Nitride and B1-Nitride/Hexagonal Boride material systems) on the thermal stability of multilayered (superlattice) coatings compared with nanocomposite coatings?
- (ii) Which superhard material systems, in addition to “Ti–Si–N” and “Ti–B–N”, possess high thermal stability?
- (iii) Is it possible to produce superhard coatings with thermal stability based on oxides, and what are the formation mechanisms of this type of coating?
- (iv) Is it possible to develop a theoretical model which can predict the thermal stability of superhard coatings?

4. Conclusions and recommendations

In the last 15 years several superhard material systems have been developed, but only two systems, “Ti–Si–N” and “Ti–B–N”, possess high thermal stability. We presented here various structures and composition of superhard coatings which exhibit similar hardness but completely different thermal stability. This seems to depend on the relationship between different mechanisms of hardness enhancement and the distinct thermal stability behavior of the superhard coatings. However, we have seen that multilayered and nanocomposite material systems fabricated by spinodal phase segregation and enhanced energetic ion bombardment are systems that exhibit significant thermal stability behavior.

The nanolayers (or nanocomposites) must have a well-defined interface of high cohesive strength, because the small grains hinder dislocation–formation and movement, and the well-defined interface hinders grain boundary sliding. Another hardness-enhancing mechanism is residual compressive stress. High compressive stress enhances the coating hardness toward superhardness, but reduces coating stability when annealed at high temperature due to stress relaxation.

The friction between the cutting tool and work piece causes intense heating, which affects the coating and substrate properties. This heat accelerates stress relaxation, recrystallization and grain growth, diffusion between the coating and substrate, and oxidation. Thus, the most important properties of a high-temperature superhard coating are:

- (i) high oxidation resistance;
- (ii) low miscibility between the coating compounds, in order to prevent diffusion between them;

- (iii) low residual compressive stress;
- (iv) low solubility at high temperatures for both the substrate and the working piece.

We can conclude, therefore, that a deeper understanding of the interaction between fabrication parameters, film-growing techniques (PVD vs. PECVD), film structures and composition is the key to understanding the thermal stability of superhard coatings.

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