First-principles quantum molecular calculations of structural and mechanical properties of TiN/SiN_x heterostructures, and the achievable hardness of the nc-TiN/SiN_x nanocomposites

V. I. Ivashchenko^a, S. Veprek^{b,*}, A.S. Argon^c, P. E.A. Turchi^d, L. Gorb^{e,f}, F. Hill^f, J. Leszczynski^g

^a Institute of Problems of Material Science, National Academy of Science of Ukraine, Krzhyzhanosky str. 3, 03142 Kyiv, Ukraine, e-mail: ivash@ipms.kiev.ua

^b Department of Chemistry, Technical University Munich, Lichtenbergstrasse 4, D-85747 Garching, Germany

^c Department of Mechanical Engineering, Massachusetts Institute of Technology, 77 Massachusetts Avenue, Cambridge, MA 02139, USA

^d Lawrence Livermore National Laboratory (L-352), P.O. Box 808, Livermore, CA 94551, USA

^g Department of Chemistry and Biochemistry, Interdisciplinary Center for Nanotoxicity, Jackson State University, Jackson, MS 39217, USA

^e Badger Technical Services, LLC, Vicksburg, MS 39180.

^f U.S. Army ERDC, Vicksburg, MS 39180, USA

* Corresponding authors: stan.veprek@lrz.tum.de Phone: +49 89 28913624,
Fax: +49 89 28913626

TiN/SiN_x heterostructures with one monolayer of the interfacial SiN_x have been investigated in the framework of first-principles molecular dynamics calculations in the temperature range of 0 to 1400 K with subsequent static relaxation. The atomic configurations, thermal stability and stress-strain relations have been calculated. Among the heterostructures studied, only the TiN(111)/SiN/TiN(111) and TiN(111)/Si₂N₃/TiN(111) ones are thermally stable. Upon tensile load, decohesion occurs between the Ti-N bonds adjacent to the SiN_x interfacial layer for TiN(001)/SiN/TiN(001) and TiN(111)/Si₂N₃/TiN(111) heterostructures, and inside the TiN slab for TiN(001)/Si₃N₄/TiN(001) and TiN(110)/SiN/TiN(110) ones. Upon shear, failure occurs in TiN near the interfaces in all the heterostructures, except for the TiN(001)/Si₃N₄/TiN(001) one, for which the plastic flow occurs inside the TiN slab. Based on these results we estimate the maximum achievable hardness of nc-TiN/Si₃N₄ nanocomposites free of impurities to be about 170 GPa.

Keywords: Superhard nanocomposites, TiN/SiN_x heterostructures, first-principles molecular dynamics, thermal stability; stress-strain relations, ideal strength, achievable hardness.

1. Introduction

Much progress in the design of superhard nanocomposites and nanolayered heterostructures consisting of nanocrystals or nanoslabs of hard transition metal nitride (TmN) and one or two monolayers (1-2 ML) of interfacial covalent compound XY (SiN_x, AlN, BN and the like), and in the understanding of their properties has been achieved during the last two decades. This is particularly true for TiN/SiN_x-based nanocomposites which exhibit superhardness of 50-100 GPa combined with high thermal stability and oxidation resistance (e.g. [1–10]). The large hardness enhancement of the nanocomposites as compared to pure TiN coatings (about 21 GPa) has been attributed to the nanometer size TiN grains, and to a SiN_x interfacial monolayer that is strengthened by valence charge transfer. This combination efficiently impedes the dislocation formation, multiplication and motion as well as other mechanisms of plasticity [11]. Strengthened grain boundaries prevent grain boundary sliding and hence increase the strength and hardness [6].

Based on the shear resistance of fcc-TiN/SiN/TiN heterostructures with 1 ML of pseudomorphic fcc-SiN, calculated by the “static” density functional theory (DFT) at 0 K, achievable hardness of nc-TiN/SiN_x nanocomposites in excess of 130 GPa has been estimated for nanocomposites with 3-4 nanometer sized randomly oriented TiN nanocrystals connected by 1 ML SiN interfacial, pseudomorphic layer [11]. When the thickness of the SiN layer increased to 2 ML, the hardness enhancement is lost as shown experimentally (see Fig. 17 in the recent review [6] and references therein), and explained by DFT calculations due to the weakening of the Ti-N bonds adjacent to the SiN interface [12-14]. However, impurities, mainly oxygen, strongly limit the achievable hardness [15], and avoid formation of the nanocomposites by impeding diffusion and, in such a way, apparently stabilizing the solid solution [16] already at a concentration of 0.7-0.8 at.% (7000-8000 ppm). Therefore the very high achievable hardness can be obtained only if the impurities are few 100 ppm or less [6,15,16].

The formation and stability of the epitaxial interfaces in TiN/SiN_x heterostructures have been studied in Refs. [5,7-10]. Hultman *et al.* showed that the SiN_x layer could be crystalline, provided its thickness does not exceed few monolayers [7]. The SiN_x layers were heteroepitaxial face-centered cubic in the TiN(001)/SiN nanolaminates with the thicknesses of SiN_x layers (l_{SiN}) less than 9 Å (~4.5 ML), and became amorphous when l_{SiN} exceeded 9 Å [5]. Hu *et al.* [10] showed that SiN_x, being amorphous as a single film, became crystalline in TiN/SiN_x/TiN multilayers when the thickness of the SiN_x layers was less than 0.7 nm because of the “template effect”. Iwamoto and Tanaka investigated the interfaces between Si₃N₄ brazed with TiN particles prepared at relatively high temperature of 1173 K. They found that the main crystallographic orientation relationship between Si₃N₄ and TiN was (10-10)Si₃N₄ || (1-11)TiN [17].

The TiN/SiN_x heterostructures and interfaces have been widely investigated in the framework of different first-principles calculations [11–14,18–24]. Using DFT at 0 K, Zhang *et al.* have shown that the heteroepitaxial structure of the TiN(111)/B1-SiN and TiN(001)/B1-SiN interfaces has been preserved after the structural relaxation under the periodic boundary conditions [11–13]. The topology of the semicoherent TiN(111)/β-Si₃N₄ interface was found to change by forming a plane with Si-Si bonds that were absent in the initial structure before relaxation [11]. In Ref. [14] these researchers showed that the (111) and (110) B1-SiN-like interfaces are stable against finite distortion, while the B1-SiN(001) interface is unstable against a small displacement of Si atoms, but it was stabilized by 12 % distortion in the [110] direction. The researchers from Linköping University reported that the B1-SiN(001) is dynamically unstable [18]. The distortion of Si atoms by 12% in the [110] direction led to reducing the total energy [19] in agreement with the results of Zhang *et al.* [14], but it did not remove the phonon instabilities [19]. The (111) interface has been dynamically stable [18,19]. However, both interfaces are unstable with respect to formation of Si vacancies [19]. Marten *et al.* have suggested an atomic arrangements of the layer phase to explain the apparent epitaxial TiN(001)/SiN_x interfaces [20]. It was shown that the 1 ML B3 and 3 ML B3-D0₂₂ -derived SiN_x interfaces are both dynamically and thermodynamically stable with respect to vacancy formation.

The stability of experimentally observed, thermodynamically stable TiN/Si₃N₄ interfaces, such as TiN(111)/Si₃N₄(10-10) and the like [17] have been theoretically investigated in Refs. [21–23] by means of density functional theory (DFT) calculations for heterostructures consisting

of SiN_x interfacial layers between two ten-layer thick $\text{TiN}(111)$ slabs. For nitrogen-rich conditions, the so-called “ β -like $(1\times 3)\text{-Si}_2\text{N}_3$ ” structure involving tetrahedral N-Si-N bonding was most favorable, while for nitrogen-poor conditions a $(1\times 1)\text{-TiSi}$ structure involving octahedral Ti-Si-Ti bonding was preferred [22].

The response of the TiN/SiN_x heterostructures to imposed tensile and shear strains was theoretically examined in Refs. [11–14,21,23], and its degradation by oxygen impurities in Ref. [23]. It was shown that the valence charge transfer from TiN to SiN_x causes Friedel oscillations of the valence charges which, in turn, leads to a weakening of the Ti-N bonds in the vicinity of the SiN_x interfaces. As a result, the ideal strengths of the heterostructures decreased as compared to those of perfect TiN crystal [11-14].

All these theoretical studies have been performed by means of “static” DFT at 0 K for small scale heterostructures of 16-20 atoms. This is serious limitation because thermally-induced effects and transformations cannot be seen. Therefore, in our recent work [24] we performed first-principles quantum molecular dynamic (QMD) studies of this system at elevated temperatures, however limited to the structural properties and stability of the $\text{TiN}(001)/\text{SiN}_x/\text{TiN}(001)$ and $\text{TiN}(111)/\text{SiN}_x/\text{TiN}(111)$ heterostructures. In present work we extend the first-principles QMD studies to other interfacial systems, such as $\text{TiN}(110)/\text{SiN}_x/\text{TiN}(110)$, in order to investigate their stability, and deformation modes and failure upon tensile and shear strain. The stress-strain relations, which are calculated and presented in this work, yield the shear strengths of the interfaces. These are subsequently used to estimate the maximum achievable hardness of the nanocomposites free of impurities. The advantage of the first-principles QMD is that it allows one to perform such studies at elevated temperatures.

Some of the interfacial layers, such as SiN , are thermodynamically unstable at macro-scale, and should decompose according to the reaction $4\text{SiN} \rightarrow \text{Si}_3\text{N}_4 + \text{Si}$. However, it has been shown that for example the (111) interfacial monolayer of SiN between TiN slabs is stable even upon annealing at a high temperature, probably because of kinetic reasons at the nano-scale [24]. Thus, interfacial structures which are thermodynamically unstable at macro-scale should not be ruled out in the nanocomposites at nano-scale, and therefore will be also considered in the present work.

The paper is organized as follows. In Sec. 2, the geometry of the interfaces and details of our first-principles QMD simulations are described. Sec. 3 contains the results and a discussion, and in Sec. 4 the conclusions of this work are briefly summarized. The reader who is not familiar with the first-principles DFT and QMD techniques can go directly to Sect. 3 because we tried to write it in self-consistent manner.

2. Computational details

For the study of the properties of the TiN(001)/1 ML B1-SiN/TiN(001) heterostructure, we considered 96-atom supercells constructed of the $(2 \times 2 \times 3)$ B1(NaCl)-TiN cubic unit cells, each containing 8 atoms. The TiN(111)/1 ML B1-SiN/TiN(111) heterostructure consisted of the 54-atom $(3 \times 3 \times 1)$ supercells, derived from the 6-atom B1-TiN hexagonal unit cells with $[1/2 \ 1/2 \ 0]$, $[0 \ 1/2 \ -1/2]$ and $[1 \ 1 \ 1]$ as the **a**, **b** and **c** basis vectors, respectively. The interfacial SiN monolayer has been introduced by replacing Ti atoms with Si atoms in the central lattice plane of the given supercell. A similar procedure was used to construct the initial 105-atomic TiN(111)/Si₃N₄-like heterostructure, abbreviated as “Si₂N₃”, because of the true stoichiometry of the interfacial layer that is not exactly Si₃N₄. The interface was introduced by replacing one TiN layer with Si₃N₄-like layer. The 96-atom TiN(110)/SiN heterostructure was represented by the $(2 \times 3 \times 4)$ supercell, derived from the B1-TiN tetragonal unit cells each containing 4 atoms. The notation and structural characteristics of all the initial heterostructures under consideration are summarized in Table 1. All the heterostructures consist of several parallel layers aligned perpendicular to the c-direction, one of which is the SiN_x interfacial layer. To clarify a possibility of the formation of stable Si₃N₄-like configurations by introducing Si vacancies we removed two Si atoms from the SiN(001), SiN(110) and SiN(111) interfacial layers (cf. Table 1). We verified in our earlier work [24] that such supercells are sufficiently large to provide reliable results within an acceptable computing time.

The QMD calculations were performed with the code “quantum ESPRESSO” [25] using periodic boundary conditions and the generalized gradient approximation of Perdew, Burke and Ernzerhof [26] for the exchange-correlation energy and potential. Vanderbilt ultra-soft pseudo-potentials were used to describe the electron-ion interaction [27]. The criterion of convergence for the total energy was 10^{-6} Ry/formula unit (i.e. $1.36 \cdot 10^{-5}$ eV/formula unit). In order to speed

up the convergence, each eigenvalue was convoluted by a Gaussian with a width $\sigma = 0.02$ Ry (0.272 eV).

All initial structures were optimized by simultaneously relaxing the supercell basis vectors and the atomic positions inside the supercell using the Broyden-Fletcher-Goldfarb-Shanno (BFGS) algorithm [28]. The QMD calculations of the initial relaxed heterostructures were carried out at 1400 K with fixed unit cell parameters and volume (NVT ensemble, constant number of particles-volume-temperature) for 3 ps. In all QMD calculations, the time step was 20 atomic units (about 10^{-15} s). The system temperature was kept constant within about 20 K by rescaling the velocity. The variation of the total energy was controlled during each QMD time step. All structures reached their time-averaged equilibrium during the initial simulation time of about 1 ps, and afterwards, the total energy of the structures fluctuated only slightly around that equilibrium value. In large-scale QMD simulations, the chosen reduced energy cut-off 30 Ry (408 eV) and the k-points mesh (Γ point) were used in order to save computation time without compromising accuracy. The justification of such an approach was verified in Refs. [24,29]. The temperature of 1400 K has been chosen because, under these conditions, a fast equilibration occurs, and it is also a representative value for the deposition and applications of the coatings as wear protection on tools. Afterwards, the heterostructures have been quenched to 0 K where their properties have been studied. The rate of the cooling had no significant effect on the final structure.

After QMD equilibration, the geometry of all heterostructures was optimized by simultaneously relaxing the supercell basis vectors and the positions of the atoms inside the supercell using the BFGS algorithm [28]. The Monkhorst-Pack [30] (2 2 2) mesh (4 k -points) was used. The relaxation of the atomic coordinates and of the supercell was considered to be complete when atomic forces were less than 1.0 mRy/Bohr (25.7 meV/Å), stresses were smaller than 0.05 GPa, and the total energy during the structural optimization iterative process was changing by less than 0.1 mRy (1.36 meV).

The tensile stress-strain relations were calculated by elongating the supercells along the c -axis [(001)-direction] in an incremental step, followed by fixing the c basis cell vector and simultaneously relaxing the a - and b -basis cell vectors and the positions of the atoms within the supercell. The shear stress of the heterostructures under shear strains was calculated as follows: first an incremental shear distortion was imposed, then the basis supercell vectors orthogonal to

the applied strain and the atomic coordinates were relaxed. For both tensile and shear strains the structural parameters at a previous step were used to calculate the Hellmann-Feynman stress for the next step. In these calculations, structural relaxations were performed by using damped dynamics [25].

The calculations of the stress-strain relations have been done with rigid atomic structure, i.e. at 0 K, in order to save computational time. Based on the present results, the calculations at a finite temperature will be done by first-principles QMD only for few selected representative decohesion and slip systems, because these calculations require orders of magnitude larger computational effort. Such calculations are not available yet for any system [29]. Therefore, we present in the Appendix A simple estimate to show that the weakening of the ideal strength at about 300 K will be negligible, of few %.

The above-described pseudopotential procedure was used to study the phonon spectra of the TiN/SiN heterostructures in the framework of the density-functional perturbation theory described in Refs. [25,31]. To save computation time, the 12-atomic unit cells that represent the TiN(001)/SiN/TiN(001), TiN(110)/SiN/TiN(110) and TiN(111)/SiN/TiN(111) heterostructures with the heteroepitaxial interfaces were used. Prior to the phonon structure calculations, all initial heterostructures were optimized using the BFGS procedure. The parameters of the calculations of the 12-atomic heterostructures are summarized in Table 2. The phonon density of states (PHDOS) was calculated with the tetrahedron method implemented in the “Quantum-ESPRESSO” code [25].

3. Results and discussion

3a. Calculation of stress-strain relations, deformation and failure modes

A dynamic (thermal) instability of a structure means that phonons, which are driving the structural transition, are amplified, i.e. the phonon vectors have imaginary parts which is expressed as negative frequencies [32]. Figure 1 shows the phonon densities of states for the SiN(001)-12, SiN(110)-12 and SiN(111)-12 that represent the interfacial layers between the TiN slabs. It is seen that only the SiN(111)-12 heterostructure does not show negative frequencies, i.e. it is dynamically stable. The SiN(001)-12 and SiN(110)-12 show negative frequencies which means that these interface are dynamically unstable and will not be preserved at finite

temperature. This finding is confirmed by the results of QMD simulations for the TiN/SiN_x heterostructures presented below.

In order to study the ideal tensile and shear strengths we calculate the stress-strain relationships for the TiN/SiN_x heterostructures as outlined in Sect. 2. These relations and atomic configurations are shown in Figs. 2, 3 and 4, and the ideal strengths and critical failure strains are summarized in Table 3. We shall now analyze these heterostructures according to their symmetry.

SiN(001) and Si₃N₄(001): Figure 2 shows the stress-strain curves for the (010)[001] and (001)[010] slip system and for the [001] tensile load. As expected, the behavior of the SiN_x(001) interfaces depends on temperature. At high temperatures, they represent an aggregation of the SiN₄ and SiN₆ distorted units. Detailed analysis of the temperature evolution of these interfaces was done in Ref. [24]. We also note that, as expected, the ideal shear (σ_S) and tensile (σ_T) strengths of bulk TiN are higher than those of the (001) heterostructures (cf. Table 3, Figs. 2a,b). The smallest σ_S is found for B1-SiN because of its inherent instability. The values of σ_S and σ_T for the SiN(001) heterostructures are higher for the heteroepitaxial interface at 0 K (ZT) than for that reconstructed at 1400 K (HT). Although the formation of Si₃N₄(001) interfacial layer results in higher shear resistance, it displays a lower decohesion strength upon tensile load. Figure 2a shows that the resistance of the Si₃N₄(001) heterostructure under the shear perpendicular to the interface (slip system (010)[001]) is slightly higher than that under the shear directed parallel to the interfacial layer (slip system (001)[010]).

As mentioned in Sect. 1, the SiN(001) heterostructure is unstable with respect to the formation of interfacial silicon vacancies [19] with a formation energy of a single Si vacancy (E_V) of -2.090 eV/atom [24]. Thus, the formation of silicon vacancies should strengthen the interface. An analysis of the atomic configurations of the (001) heterostructures under shear and tensile strains, presented in Figs. 2c and 2d, shows that the failure of the SiN(001) occurs near the interface, whereas the failure of Si₃N₄(001) occurs within the TiN slab. Thus, for the formation of the strong (001) grain boundaries the composition should be close to Si₃N₄, in agreement with experiment [6,10]. According to our results, the formation of the heteroepitaxial SiN(001) layer is unlikely because the Si atoms will form four-fold coordination to the neighbor N atoms (see also Ref. [14]). Thus, our QMG studies show that the structure of the SiN(001) interface is much more complex than what has been reported in the literature so far [5,7].

SiN(110) and Si₄N₆(110): As in the case of the (001) systems, the ideal shear and tensile strengths of the SiN(110) heterostructures are lower than those of TiN (cf. Table 3). The stress-strain curves for the ZT and HT SiN(110) heterostructures are very similar (cf. Figs. 3a,b), because the SiN(110) interface is only slightly modified with increasing temperature. As one can see in Fig. 3c for $\epsilon=0$, the Si atoms move along the SiN(110) interface in such a way as to reduce their coordination to five-fold bonding to nitrogen. Figure 3c demonstrates that, for the (110)[-110] slip system, which is the easy slip system in the B1 structure, the shear occurs by means of the shift of the TiN slabs parallel to the interface in the [-110] direction. During the slip, the Si-N bonds between the TiN and SiN planes are deformed and their number changes. Failure takes place when the number of these bonds reaches a minimum and the Si atoms form strongly distorted SiN₄ units. The same deformation paths is found for the (1-10)[110] shear perpendicular to the interface (cf. Fig. 3c, $\epsilon=0.12$). Consequently, the ideal shear strengths for both sliding systems are similar (cf. Table 3). The failure of the SiN(110) heterostructure under tensile strain along the [110] occurs inside the TiN slab.

To investigate the (110) interface with the atomic configuration close to that of Si₃N₄, we removed two Si interfacial atoms from the SiN(110) heterostructure. The vacancy formation energy amounts to $E_v = -1.774$ eV/atom. The substoichiometric HT-Si₄N₆(110) interface consists of five-fold coordinated Si atoms, as in the case of the stoichiometric HT-SiN(110) heterostructure (not shown here). Figures 3 a, b show that the ideal shear and tensile strengths of the HT-Si₄N₆(110) are lower than those of the stoichiometric heterostructure, which shows that the formation of Si vacancies weakens the SiN(110) heterostructure. The decohesion under both tensile and shear strains occurs near the Si₄N₆(110) interfacial layer. Strongly distorted SiN₄ units form before the failure as in the case of the SiN(110) interface (not shown here).

Si₂N₃(001), SiN(111) and Si₇N₉(111): In Ref. [24] we have shown that the 1 ML SiN(111) interfacial layer between the TiN slabs is stable even at high temperatures close to the melting point, and attributed it to kinetic constraints. This is confirmed in the present study and extended also to the Si₂N₃(111) interfacial layer. In Figs. 4a, b we see that, as expected, the ideal shear and tensile strengths of the Si₂N₃(111) and SiN(111) heterostructures are lower than those of bulk TiN, and the SiN(111) heterostructure is stronger than the Si₂N₃(111) one. The SiN(111) interfacial layer consists of the SiN₆ units whereas SiN₄ units are found in Si₃N₄ interfacial layer. Moreover, the phonon spectrum of B1-SiN with lattice parameter of TiN (i.e. interfacial layer

between TiN slabs) has soft modes with negative frequencies for both (001) and (111) interfacial layers, but the frequencies become positive for the (111) heterostructure with lattice parameter smaller than 0.39 nm (see Fig. 6 in Ref. [37]), i.e. this heterostructure becomes stable. Indeed, as seen in Fig. 4d, the Si-N bonds become shorter approaching the critical value of the Si-N bond length for which the frequencies of the soft Λ_3 [$2\pi/a(1/8,1/8,1/8)$] mode in B1-SiN(111) become positive (see Fig. 6 in [37]), which also makes the TiN(111)/SiN/TiN(111) heterostructure dynamically stable (cf. Fig. 1). This shortening of the Si-N bonds is driven by the higher electronegativity of Si as compared with Ti (1.8 and 1.5, respectively) and kinetically activated by the thermal movement.

Let us now analyze the deformation and fracture upon shear and tensile loads as shown in Figs. 4c, d. In the $\text{Si}_2\text{N}_3(111)$ and SiN(111) heterostructures, the (111)[1-10] shear occurs by the deformation of the SiN_4 and SiN_6 groups, respectively, without breaking the Si-N bonds. The failure of the Si_2N_3 heterostructure upon tensile strain takes place by the delamination inside the TiN slab. Simultaneously, the Si-N bonds in the direction of the tensile strain are elongated (cf. Fig. 4c). Upon a tensile load in the [111] direction, the SiN(111) heterostructure shows an amazing strength of 66.3 GPa (cf. Fig. 4b, Table 3). This high strength is probably due to the formation of the SiN_4 tetrahedra that remain stable upon decohesion, which occurs between the Ti-N bonds adjacent to the SiN interfacial layer (cf. Fig. 4d).

Interestingly, the substoichiometric $\text{Si}_7\text{N}_9(111)$ heterostructure, that has been formed from the SiN(111) by introducing Si vacancies with formation energy of $E_v = -0.461$ eV/atom, displays lower shear and tensile strengths as compared with the SiN(111) (see Fig. 4a, b). Thus, Si vacancies are weakening also the (111) interface. The shear and tensile failure modes of the $\text{Si}_7\text{N}_9(111)$ heterostructure are similar to those of the SiN(111) (not shown here).

We have shown that all SiN-like heterostructures considered here are unstable with respect to a formation of Si vacancies. Nevertheless, we suppose that, under nitrogen-rich conditions, SiN_x interfacial layers with compositions close to stoichiometric one can be formed [38].

A comparison of the calculated values shown in Table 3 with those obtained in other theoretical work [12,14,33-36] shows relatively good agreement with only small differences. In particular, for the (110)[1-10] and (111)[1-10] shear strains we obtain ideal strengths that are lower than in other calculations [33-36]. This discrepancy can be explained by the fact that we used larger simulation cells compared to those selected in other publications. It should be also

noted that the small divergence of our values from those calculated in other works is encouraging because the previous calculations have been done by means of the DFT at 0 K whereas in our present study we used the first-principles QMD in order to perform the simulations of the heterostructures at finite temperature.

3b. Achievable hardness of the nc-TiN/Si₃N₄ nanocomposites

As mentioned in Sect. 1, there is no dislocation activity in the 3-4 nm sized TiN nanocrystals, and the 1 ML interfacial Si₃N₄-like layer is strengthened by valence charge transfer from the TiN. Extensive studies of the nc-TiN/Si₃N₄ nanocomposite by means of high-resolution transmission electron microscopy (HR TEM) of a number of samples (several tens of HRTEM micrographs per each sample) showed that the TiN nanocrystals are free of any defects, in particular of dissolved Si atoms [39]. This is in agreement with the well documented fact that pure and stoichiometric transition metal nitrides and Si₃N₄ are immiscible [40]. The impurity content in these samples was very low, only few 100 ppm. High-pressure X-ray diffraction (XRD) study has shown that the interfaces are the carrier of the plastic flow in the nanocomposites, whereas the TiN nanocrystals deform only elastically [41]. Therefore it is justified to take the shear resistances of these TiN/SiN_x/TiN interfaces, calculated by the first-principles method, as the plastic resistance of the nanocomposites when the plastic deformation occurs under the indenter. These resistances are of course smaller than the ideal shear strength of a TiN single crystal. However, the correctly measured, load-invariant hardness is the average pressure beneath the indenter under the conditions of fully developed plasticity where no single crystal exists. Therefore, the material under the indenter must be full of flaws and its “shear resistance” is orders of magnitude smaller than the ideal shear strength. One should note that the strength of engineering materials is orders of magnitude smaller than the ideal strength of their perfect crystals because of the presence of flaws [42,43].

In Ref. [11] we have shown that taking the shear strength of the pseudomorphic SiN interfaces calculated by the “static” DFT at 0 K, the achievable hardness can be significantly above 100 GPa. Because the present QMD calculations provide much more reliable values of the structure and shear resistance of the interfaces including the stoichiometric Si₃N₄-like one, we shall estimate the achievable hardness using these values, following the procedure outlined in [11]. We disregard the substoichiometric interfaces derived from the pseudomorphic SiN by

formation of Si vacancies because, as it has been shown above, these are weak and will most probably undergo nitriding to Si_3N_4 -like interfacial layer during deposition under sufficiently high nitrogen activity (note, that, due to the mathematical constraints, the first-principle calculations are conducted for a closed system (NVT ensemble, Sect. 2) whereas during the deposition the system is “open”, see remark [38]).

According to Meyer [44], indentation hardness is the average pressure beneath the indenter under conditions of fully developed plasticity. At the start of the indentation, the initial deformation at low load is elastic with a maximum shear stress developing under the indenter tip in a depth of 50 % of the contact radius between the indenter and the material, where the plastic flow commences [45]. Therefore one has to account for the pressure-enhancement of the shear resistance of the interfaces calculated above. The enhanced resistance, σ_s , at pressure p (called the “strength differential effect”) is given by equation (1).

$$\sigma_s(p) = \sigma_s(0) + \beta \cdot p \quad (1)$$

where the shear resistance $\sigma_s(0)$ under zero pressure calculated by the present QMD, is enhanced linearly, and β is the strength differential effect coefficient (see [11] and references therein). The values of $\beta \approx 0.1\text{-}0.3$, obtained experimentally in a number of publications have been summarized by Olejnik in his review [46]. We shall use a conservative value of 0.15. The pressure at which the plastic flow beneath the indenter commences amounts to $p_{\text{max}} = 2.58 \cdot \sigma_s(0)$ [45]. Thus, the plastic resistance of the interfaces is, upon the onset of plastic flow, enhanced by a factor of $[1 + 0.15 \cdot 2.58] \approx 1.39$.

The zero-pressure shear resistance (ideal shear strength) of the stable interfaces calculated above varies between about 15 and 32 GPa (Fig. 3 & 4). We take as a conservative average value 20 GPa, but we note that, under fully developed plastic flow, all interfaces, even the strongest ones, have to shear to meet the compatibility condition of constant volume during the deformation. Thus, the conservative average value of the shear resistance of the interfaces amounts to about

$$\sigma_s(p) \approx 27.8 \text{ GPa}. \quad (2)$$

We know from a number of XRD [1,2,6] and electron diffraction [39] studies that in the pure nanocomposites with fully segregated TiN and Si_3N_4 , the TiN nanocrystals are randomly oriented. Consequently, the interfaces sliding under the plastic flow are also randomly oriented, and their contribution to the overall shear resistance of the assembly of grains has to be

averaged. The problem is similar to the averaging of the shear resistance of different crystallographic slip systems in grains of a randomly oriented polycrystal to obtain its uniaxial plastic resistance. (Note that a single crystal will shear along the easiest slip system as illustrated e.g. by Figs. 3.3 and 3.5 in Ref. [42]. Therefore, a randomly oriented polycrystal is stronger than a single crystal.) The solution of this problem has been provided by Sachs [47] who calculated the uniaxial tensile yield strength Y of a polycrystal with averaged shear resistance σ_s to be

$$Y = 2.24 \cdot \sigma_s(p), \quad (3)$$

which for the nanocomposites gives $Y \approx 62$ GPa. (For more detailed discussion of the applicability of the Sachs analysis we refer to the paper [11].)

The relationship between the indentation hardness and tensile yield strength, $H = C \cdot Y$, has been subject of many studies back to Prandtl [48]. The “constraint” factor $C \approx 3$ has been found for metals [45], but it decreases to about 2 for silicate glasses (which deform to large extent by compaction) and is close to 1 for polymers and elastomers. We refer to Appendix B in the recent review [6] which provides a detailed summary of the literature (see also a remark [49]). Non-linear finite element modeling of the indentation into the nanocomposites provided the value of about $C \approx 2.8$ [54]. This value is supported by recent experimental study of Wheeler et al. who found for a several transition metal nitride coatings values of constraint factor between 2.63 and 3.09 for AlCrTiSiN and AlCrSiN nanocomposites, respectively (see Table 1 in Ref. [53]). Thus, the theoretically achievable hardness of these materials is

$$H = 2.8 \cdot Y \approx 173 \text{ GPa}. \quad (4)$$

This value is of course much higher than the maximum hardness of about 70 GPa obtained experimentally for the long-term stable quasi-binary nc-TiN/Si₃N₄ nanocomposites [16], and of about ≥ 105 GPa for the quasi-ternary nc-TiN/Si₃N₄/TiSi₂ nanocomposites [55] that are, however, not long-term stable [6,16]. The reasons for the lower hardness achieved experimentally are impurities, mainly oxygen, because even in the best prepared coatings the oxygen impurity level has been at a few 100 ppm. We refer to Refs. [6,15,16] for further discussion.

3c. How to understand such a high hardness and how can it be measured?

A critical reader may ask how can a nanocomposite consisting of TiN ($H \approx 21$ GPa) and Si₃N₄ ($H \approx 18$ GPa) have such a high hardness, and how can a hardness ≥ 105 GPa be measured

with diamond indenter which has a similar or even lower hardness. The answer to the second question is relatively simple: Upon indentation, the diamond indenter is loaded in pressure whereas the material being indented is loaded in shear (see e.g. Fig. 13.8 in Ref. [43] p. 454). Diamond (like many other materials) sustains about 8-times higher load under pressure than under shear [56]. Therefore, the very high hardness of nano-twinned cubic boron nitride of 108 GPa [57] and nano-twinned Diamond of 200 GPa [58] could be measured using a diamond indenter. Of course, upon indentation into such a hard material an initially sharp diamond tip will plastically deform locally, becoming dull, and its “radius” will increase with increasing number of indentations. However, after 15 to 25 indentations into such material it will stabilize with a radius of 0.5 to 0.7 μm , and upon further indentation it will deform only elastically as shown by experiment [59] and confirmed by non-linear finite element modeling [54]. (We write the “radius” in parentheses because the shape of the deformed tip is not exactly spherical [54].)

The very high hardness of the nanocomposites is understandable by careful reading Sect. 3b and the early paper [11], but a few more explanatory remarks are appropriate. With decreasing crystallite size the strength and hardness of materials increases because the grain boundaries impede the motion of dislocations and their multiplication as well as plastic flow by other mechanisms, such as twinning and the like. However, when the crystallite size approaches 10 to 20 nm, the hardening usually changes to softening (called “grain boundary shear” or “sliding”, or “inverse Hall-Petch”) because the fraction of the “softer” material within the grain boundaries strongly increases [6,16]. Therefore this crystallite size is called “The Strongest Size” [60,61]. This strongest size limit can be shifted to smaller crystallite size by forming low-energy grain boundaries, such as twins [57,58] or stacking faults [62], and the strength and hardness can be further increased. As explained in Sect. 3b, the 1 monolayer thin SiN_x interfacial layer in the nc-TiN/ Si_3N_4 nanocomposites is strengthened by valence charge transfer so that its de-cohesion strength is much higher than the ideal tensile strength of Si_3N_4 single crystal (see Ref. [21,22]). Therefore, the crystallite size of the nc-TiN reaches very low value of 3-4 nm and their strength approaches the ideal one. Consequently, the hardness of the nanocomposites reaches high values limited presently by impurities to about 70 GPa for the stable quasi-binary nc-TiN/ Si_3N_4 coatings [16] and to more than 105 GPa for the quasi-ternary nc-TiN/ Si_3N_4 / TiSi_2 one which are, however, stable only on the time-scale of several months and lose hardnes

afterwards due to an instability of the metastable phases of TiS_2 which form at relatively low deposition temperature of 550 °C, as reported in Ref. [2] and discussed in Refs. [6,16].

CONCLUSIONS

We have carried out first-principles molecular dynamics calculations of the stability of variety of interfaces in the TiN/SiN_x heterostructures and their ideal tensile and shear strength. The $\text{SiN}(001)$ interface is dynamically unstable in agreement with earlier DFT studies at 0 K, and undergoes transformation at finite temperature. The $\text{SiN}(110)$, $\text{Si}_3\text{N}_4(001)$, $\text{SiN}(111)$ and $\text{Si}_2\text{N}_3(111)$ are stable, or change insignificantly with temperature. Therefore they may occur in the nanocomposites, albeit that the SiN stoichiometry is thermodynamically unstable at macro-scale.

The calculated stress-strain relations of the heterostructures show that their ideal shear and tensile strengths are, as expected, lower than those of a perfect TiN crystal. Under the conditions of fully developed plasticity, the strengthened interfacial SiN_x layers lead to hardness enhancement in heterostructures and nanocomposites because of their impeding effect on the formation, multiplication and movement of dislocations and other mechanisms of plastic flow.

Heterostructures with different interfacial layers show differences in the modes of tensile and shear deformation and failure: in the majority of the heterostructures studied here the failure occurs by breaking of the Ti-N bonds adjacent to the SiN_x interfacial layer, but in some cases the Ti-N bonds inside the TiN slabs fail. However, in all cases the SiN_x interfacial layer remains preserved. The highest ideal tensile strength, which has been found for the $\text{SiN}(111)$ heterostructure, is due to the formation of the SiN_4 fragments at the interface during elongation.

The formation of silicon vacancies stabilizes the $\text{SiN}(001)$, $\text{SiN}(110)$ and $\text{SiN}(111)$ heterostructures, but it influences the mechanical properties of the heterostructures in different ways: in the case of the $\text{SiN}(001)$ it results in strengthening the interface, whereas for other heterostructures it leads to weakening.

The calculated shear strengths of the interfaces have been used to estimate the achievable hardness of the $\text{nc-TiN}/\text{Si}_3\text{N}_4$ nanocomposites by accounting for their enhancement due to the pressure developed beneath the indenter upon onset of plasticity, the Sachs averaging for randomly oriented TiN nanocrystals, and constraint factors obtained by means of non-linear finite element modeling, which are in agreement with recent experimental data. The resultant

hardness of an “ideal” nanocomposite of about 170 GPa is much higher than the practically achieved one because, in the later case, it is limited by impurities. However, this estimate shows that long-term stable hardness of ≥ 100 GPa should be possible in the nc-TiN/Si₃N₄ nanocomposites if the impurities could be decreased below 100 ppm.

Acknowledgments

This work was supported by the STCU contract, No. 5964. The work of P. T. was performed under the auspices of the U. S. Department of Energy by the Lawrence Livermore National Laboratory under contract No. DE-AC52-07NA27344. The authors are grateful to the directorate of the Summer Institute at Jackson State University for financial support and the opportunity to perform large-scale calculations. S.V. thanks the company SHM for financial support. A. S. A. acknowledges support from the Mechanical Engineering Department at MIT. Our thanks are due to Dr. Maritza Veprek-Heijman for valuable comments to the manuscript.

Appendix A

The temperature dependence of the ideal strength

As mentioned above, the calculation of the ideal strength at final temperature can be done only by means of first-principles QMD which, however, requires orders of magnitude more computational power than the “static” DFT. This work is in progress for few typical systems selected on the basis of the present results at 0 K, but we shall need a lot of time to complete it. Therefore we shall present here a simple estimate of the possible weakening of the ideals shear strength that is relevant for the plastic flow. The simplest estimate of the ideal shear strength can be obtained from the Frenkel’s formula for the ideal shear strength, σ_s , in the direction parallel to crystal planes separated by a distance h with atoms within those planes separated by a distance a , $\sigma_s = Ga/2\pi h$ (G is the shear modulus) [63]. For temperature between 0 K and about 300 K, the thermal expansion, i.e. changes of a and h , can be neglected, because for an isotropic material the expansion of a and h cancel out, and for an anisotropic system they will equal to $\Delta\alpha \cdot T$ (here, $\Delta\alpha$ is the difference of the thermal expansion coefficients in the relevant directions, and T is the temperature). Considering the typical values of α , it is clear that for temperature of several hundred K this contribution will be less than 1%, i.e. it can be neglected. Thus the thermal dependence of σ_s can be approximated by thermal dependence of the shear modulus G ,

which is, for the temperature range considered here and for refractory nitrides, such as TiN and Si₃N₄, expected to be low. Because we are not aware of any measured values of the temperature dependence of shear moduli of these materials, we use, for illustration, the known dependence of Yonug's modulus, E , as shown e.g. in Fig. 1.2d of Ref. [42]. One can see that for homologous temperature $T_H = T/T_m \leq 0.5$ (T_m is the melting point), the decrease of the Young's modulus does not exceed few %. Because the temperature dependence of the Poisson's ratio, ν , is also small, the decrease of the value of the shear modulus $G = E/2(1+\nu)$, and of the concomitant ideal shear strength will also be only few %. Also more detailed estimates show that the decrease of the ideal shear strength between 0 K and 300 K should not exceed several % [63]. Thus, the ideal strength of the nc-TiN/Si₃N₄ nanocomposites should be close to the values calculated in this work at 0 K, and the resultant hardness should be significantly above 100 GPa even at finite temperature.

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deform to large extent by compression, and for polymers and elastomers, but not for the ceramic nanocomposites where the complex flow of materials including flow towards the surface of the specimen being indented (see Fig. 29 in Ref. [6]) is described more correctly by slip-line-fields (see e.g. Fig. 13.8 in Ref. [43] and Fig. 70 in Ref. [52]). It should be emphasized, that Wheeler et al. [53] reported constraint factor between 2.63 and 3.09 for AlCrTiSiN and AlCrSiN nanocomposite coating, respectively, based on experimental measurements of hardness H and yield strength Y , free of any model. Therefore the value of 2.0, as suggested by Liu et al., cannot be considered as representative of high-quality nanocomposites, whereas the value of 2.8 is much better justified.

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Denotation	Structure	N_a	N_L	Supercell configuration	Symmetry of initial cells	Si- N_i
SiN(001)	Ti ₄₀ N ₄₀ (001)/Si ₈ N ₈	96	5	2×2×3	Tetragonal	Si-N ₆
Si3N4(001)	Ti ₄₀ N ₄₀ (001)/Si ₆ N ₈	94	5	2×2×3	Tetragonal	Si-N ₆
SiN(110)	Ti ₄₂ N ₄₂ (110)/Si ₆ N ₆	96	7	2×3×4	Orthorhombic	Si-N ₆
Si2N3(110)	Ti ₄₂ N ₄₂ (110)/Si ₄ N ₆	94	7	2×3×4	Orthorhombic	Si-N ₆
SiN(111)	Ti ₁₈ N ₁₈ (111)/Si ₉ N ₉	54	4	3×3×1	Hexagonal	Si-N ₆
Si7N9(111)	Ti ₁₈ N ₁₈ (111)/Si ₇ N ₉	52	4	3×3×1	Hexagonal	Si-N ₆
Si2N3(111)	Ti ₄₅ N ₄₅ (111)/Si ₆ N ₉	105	10	3×3×2	Hexagonal	Si-N ₄

Table 1. Structure, composition, number of atoms in supercells (N_a), number of the layers in the TiN unit (N_L), supercell configurations (with respect to the simple cubic TiN unit cell), symmetry of the interface and configuration of Si atoms at the interface (Si- N_i) of all the initially selected heterostructures.

Denotation	Structure	Symmetry of the initial structures	k-mesh	q-mesh
SiN(001)-12	Ti ₅ N ₆ Si(001)	tetragonal	(4 4 2)	(12 12 3)
SiN(110)-12	Ti ₅ N ₆ Si(110)	orthorhombic	(4 8 8)	(6 12 12)
SiN(111)-12	Ti ₅ N ₆ Si(111)	hexagonal	(8 8 2)	(12 12 3)

Table 2. Noation, structure and the parameters for the calculations of the 12-atomic TiN/SiN heterostructures.

Structure	Strain	Ideal strength (GPa)	Critical strain	Ref.
(010)[001]	TiN	41.1 (35.5)	0.32 (0.28)	[33]
	ZT-SiN(001)	29.4	0.24	
	HT-SiN(001)	20.4	0.16	
	HT-Si ₃ N ₄ (001)	32.1	0.26	
(001)[010]	HT-Si ₃ N ₄ (001)	25.3	0.20	
(110)[1-10]	TiN	26.1 (29.0) (31.0) (29.1)	0.16 (0.2) (0.15) (0.21)	[33] [34] [35] [36]
	ZT-SiN(110)	17.8 (17.5)	0.16 (0.15)	
	HT-SiN(110)	17.4	0.16	
	HT-Si ₄ N ₆ (110)	11.7	0.08	
(1-10)[110]	ZT-SiN(110)	16.7	0.12	
	HT-SiN(110)	17.0	0.10	
(111)[1-10]	TiN	30.0 (35.3) (32.3)	0.24 (0.33) (0.26)	[33] [35] [36]
	HT-SiN(111)	15.4 (14.0)	0.16 (0.08)	
	HT-Si ₇ N ₉ (111)	10.0	0.08	
	HT-Si ₂ N ₃ (111)	13.0	0.12	
[001]	TiN	29.4 (31.3)	0.14 (0.14)	[35]
	ZT-SiN(001)	23.3	0.16	
	HT-SiN(001)	15.8	0.08	
	HT-Si ₃ N ₄ (001)	16.9	0.16	
[110]	TiN	56.5 (53.4)	0.36 (0.36)	[35]
	ZT-SiN(110)	38.0 (38.5)	0.16 (0.15)	
	HT-SiN(110)	39.0	0.20	
	HT-Si ₄ N ₆ (110)	36.2	0.16	
[111]	TiN	102.9 (101.0)	0.44 (0.42)	[35]
	HT-SiN(111)	66.3 (60.5)	0.24 (0.17)	
	HT-Si ₇ N ₉ (111)	46.2	0.12	
	HT-Si ₂ N ₃ (111)	44.5	0.12	

* In parentheses, the values were extracted from theoretical stress-stain curves, therefore, small errors may have been introduced (~2-3 %).

Table 3. Ideal strength, critical strain and the region where the failure occurs under shear and tensile strains for TiN and the heterostructures. In parentheses, the results of other theoretical investigations are reported*.

Figure Captions

Fig. 1: Phonon density of states for the 12-atomic TiN(001)/SiN (SiN(001)-12), TiN(110)/SiN (SiN(110)-12) and TiN(111)/SiN (SiN(111)-12) heterostructures (cf. Table 2). Negative wavenumbers denote the existence of imaginary branches in the phonon spectrum.

Fig. 2: (a) Stress-strain relations in shear, and (b) stress-strain relations in tensile loading for the SiN(001) and Si₃N₄(001) heterostructures, as well as for B1-TiN and B1-SiN. The (010)[001] and (001)[010] shears are perpendicular and parallel to the interfaces, respectively. Atomic configurations of the HT-SiN(001) (c) and HT-Si₃N₄(001) (d) under the shear and tensile strains. In this figure and in other figures, the arrow indicates the shear direction. The Ti-N and Si-N bond length cutoffs are 2.5 Å and 2.2 Å, respectively.

Fig. 3: (a) Stress-strain relations in shear, and (b) stress-strain relations in tensile loading for the SiN(110) heterostructures, as well for B1-TiN. The shear (110)[-110] and shear (1-10)[110] are parallel and perpendicular to the SiN(110) interface, respectively. Atomic configurations of the HT-SiN(110) heterostructure under the shear (top) and tensile (bottom) strains are displayed in Fig. (c).

Fig. 4: (a) Stress-strain relations in shear, and (b) and stress-strain relations in tensile loading for the HT-SiN(111) and HT-Si₂N₃(111) heterostructures, as well as for B1-TiN. Atomic configurations of the HT-Si₂N₃(111) and HT-SiN(111) heterostructures under shear and tensile strains are shown in (c) and (d), respectively.

Fig. 1: Phonon density of states for the 12-atomic TiN(001)/SiN (SiN(001)-12), TiN(110)/SiN (SiN(110)-12) and TiN(111)/SiN (SiN(111)-12) heterostructures (cf. Table 2). Negative wavenumbers denote the existence of imaginary branches in the phonon spectrum.

Fig. 2: (a) Stress-strain relations in shear, and (b) stress-strain relations in tensile loading for the SiN(001) and Si₃N₄(001) heterostructures, as well as for B1-TiN and B1-SiN. The (010)[001] and (001)[010] shears are perpendicular and parallel to the interfaces, respectively. Atomic configurations of the HT-SiN(001) (c) and HT-Si₃N₄(001) (d) under the shear and tensile strains. In this figure and in other figures, the arrow indicates the shear direction. The Ti-N and Si-N bond length cutoffs are 2.5 Å and 2.2 Å, respectively.

Fig. 3: (a) Stress-strain relations in shear, and (b) stress-strain relations in tensile loading for the SiN(110) heterostructures, as well for B1-TiN. The shear (110)[-110] and shear (1-10)[110] are parallel and perpendicular to the SiN(110) interface, respectively. Atomic configurations of the HT-SiN(110) heterostructure under the shear (top) and tensile (bottom) strains are displayed in Fig. (c).

Fig. 4: (a) Stress-strain relations in shear, and (b) stress-strain relations in tensile loading for the HT-SiN(111) and HT-Si₂N₃(111) heterostructures, as well as for B1-TiN. Atomic configurations of the HT-Si₂N₃(111) and HT-SiN(111) heterostructures under shear and tensile strains are shown in (c) and (d), respectively.