Contents lists available at ScienceDirect

ELSEVIER



Materials and Design

journal homepage: www.elsevier.com/locate/matdes

Enhanced fracture toughness in ceramic superlattice thin films: On the role of coherency stresses and misfit dislocations



Antonia Wagner^{a,*}, David Holec^b, Paul Heinz Mayrhofer^a, Matthias Bartosik^a

^a Institute of Materials Science and Technology, TU Wien

^b Department of Materials Science, Montanuniversität Leoben

HIGHLIGHTS

G R A P H I C A L A B S T R A C T

- An algorithm based on elasticity theory is proposed to estimate the dislocation densities in ceramic superlattice thin films.
- The bilayer period significantly influences the misfit dislocation densities and the associated coherency stresses.
- Predictions of the apparent fracture toughness of TiN/CrN superlattices match experimental trends.
- The model reveals the potential of a superlattice structure to increase the crack growth resistance of a thin film.

ARTICLE INFO

Article history: Received 16 October 2020 Received in revised form 20 January 2021 Accepted 21 January 2021 Available online 27 January 2021

Keywords: Thin films Superlattice Misfit dislocations Residual stresses Coherency stresses



ABSTRACT

Superlattice (SL) thin films composed of refractory ceramics unite extremely high hardness and enhanced fracture toughness; a material combination which is often mutually exclusive. While the hardness enhancement is well described by existing models based on dislocation mobility, the underlying mechanisms behind the increase in fracture toughness are yet to be unraveled. Here, we provide a model based on linear elasticity theory to predict the fracture toughness in (semi-)epitaxial nanolayers. As representative of cubic transition metal nitrides, a TiN/CrN superlattice structure on MgO (100) is studied. The density of misfit dislocations is estimated by minimizing the overall strain energy, each time a new layer is added on the nanolayered stack. The partly relaxed coherency stresses are then used to calculate the apparent fracture toughness (K_{app}) by applying the weight function method. The results show that K_{app} increases steeply with increasing bilayer period for very thin SLs, before the values decline more gently along with the formation of misfit dislocations. The characteristic K_{app} vs. bilayer-period-dependence nicely matches experimental trends. Importantly, all critical stress intensity values of the SLs clearly exceed the intrinsic fracture toughness of the layer materials, evincing the importance of coherency stresses for increasing the crack growth resistance.

© 2021 Published by Elsevier Ltd. This is an open access article under the CC BY-NC-ND license (http://creativecommons.org/licenses/by-nc-nd/4.0/).

1. Introduction

A careful structural design has proven to be an effective strategy for enhancing the performance of ceramic thin films (e.g. in [1-5]).

* Corresponding author. *E-mail address:* antonia.wagner@tuwien.ac.at (A. Wagner). Particularly the alternating deposition of two or more layer materials with a periodicity in the nanometer range allows for tailored properties that exceed the inherent properties of the multilayers monolithic constituents [6].

Helmersson et al. [7] showed hardness values of up to 5560 HV (about 55GPa) for TiN/VN superlattice thin films, which is a more than 100% increase compared with single-phase TiN or VN. The nanometer-thin and

https://doi.org/10.1016/j.matdes.2021.109517

0264-1275/© 2021 Published by Elsevier Ltd. This is an open access article under the CC BY-NC-ND license (http://creativecommons.org/licenses/by-nc-nd/4.0/).

isostructured TiN and VN layers were epitaxially grown on a singlecrystalline MgO substrate by means of physical vapor deposition. For a better understanding of the mechanisms behind the high hardness values, Chu and Barnett [8] proposed a model based on dislocation glide within the individual layers and across the interfaces. Micro-mechanical tests on nitride-based superlattice thin films [9,10] further revealed an enhancement in fracture toughness. The combination of high hardness and enhanced fracture toughnesss is often mutually exclusive [11] but of high relevance for inherently brittle refractory ceramics. Both, hardness and fracture toughness, exhibit a strong dependence on the bilayer period of the superlattice and peak at a few nanometers. Unlike the hardness enhancement, the mechanisms behind the superlattice effect in terms of the fracture toughness are far less understood. Possible mechanisms are for instance coherency stresses and misfit dislocation arrays [12,13], elastic mismatch between the layer materials [14], and the change of the bonding characteristics with decreasing layer thicknesses [15,16].

Coherency stresses can reach high values in the order of tens of GPa in the absence of misfit dislocations in epitaxial nanolayers [17]. However, a fully coherent layer growth is rather unlikely for lattice mismatched heterostructures, since the formation of misfit dislocations becomes energetically favorable when a certain layer thickness is exceeded. The concept of misfit dislocations was first proposed for a misfitting monolayer grown on a crystalline substrate by Frank and van der Merwe [18] by considering the strain energy in the layer and the interfacial energy obtained by a Frenkel-Kontorowa type model. Based on this energy minimization approach, van der Merwe further calculated the equilibrium dislocation spacing in an epitaxially grown thin film [19,20]. Some years later Matthews and Blakeslee [21] derived a criterion for misfit accommodation based on mechanical equilibrium theory considering the force exerted by the misfit strain and the tension in the dislocation line in terms of the Volterra dislocation model. These models have been extended by numerous researchers, e.g. regarding elastically anisotropic material behavior, interaction between dislocations, the effect of introducing dislocations sequentially and asymmetric misfit strain [22-27]. Still, there appears to be little research on dislocation density in multilayer structures and the literature available on this topic only considers equal dislocation density in all layers or even treats the superlattice as an alloy regarding its lattice parameter [21,28,29]. Especially the influence of the architecture on the residual stress state of a superlattice thin film has not be discussed by means of a misfit dislocation model so far.

The positive effect of compressive residual stresses on the crack growth resistance is well known and has been investigated for various multilayer structures [30–33]. However, to the best of our knowledge, there have been no studies on the potential of coherency stresses and the suppression of misfit dislocations by a superlattice structure to increase the apparent fracture toughness of an inherently brittle thin films.

The objective of the present work is to elaborate the role of coherency stresses and misfit dislocations for the enhanced fracture toughness of ceramic superlattices. An algorithm to determine the misfit dislocation density and the resulting residual stress state of a (semi-)coherently grown multilayer will be presented. Based on the stress state, the fracture toughness of the system under consideration will then be calculated by applying the weight function method proposed by Bueckner et al. [34]. Adopting this procedure for cubic transition metal nitride superlattices reveals the considerable significance of coherency stresses and misfit dislocations for the bilayer-period-dependent apparent fracture toughness. Besides the qualitative analysis, the maximum potential fracture toughness enhancement for a TiN/CrN superlattice structure is discussed.

2. Method

2.1. Estimation of the misfit dislocation density in a single layer

First, the simplest configuration of a single layer deposited on a substrate is studied, see Fig. 1a. The film grows coherently up to a critical thickness, h_{crit} , at which part of the lattice mismatch between film and substrate material starts being accommodated by misfit dislocations. Based on experimental high resolution transmission electron microscopy analyses of cubic transition metal nitride thin films, e.g. by Hultman et al. [35], we presume a network of orthogonal edge-type dislocation arrays as depicted in Fig. 1a. We further assume, that the orthogonal dislocations form simultaneously. Hence, a uniform biaxial stress state is considered at any point of the layer addition. With growing layer thickness the mean distance between dislocations *d* is reduced, i.e. the misfit dislocation density $Q = \frac{1}{d}$, with unit cm⁻¹, increases. The density of misfit dislocations at the interface is calculated by minimizing the overall elastic energy in the system with respect to *Q*. The elastic energy per interface area $\frac{U(Q)}{A}$ of the system is given by the sum of the energy due to the mean strain in the layer $\frac{U_{\text{strain}}(Q)}{A}$ and the dislocation energy resulting from the local dislocation stress field $\frac{U_{\text{disloc}}(Q)}{2}$:

$$\frac{U(Q)}{A} = \frac{U_{\text{strain}}(Q)}{A} + \frac{U_{\text{disloc}}(Q)}{A}.$$
(1)

For evaluating $\frac{U_{\text{strain}}(Q)}{A}$, the stress state of the system as a function of Q has to be defined. Within this treatment the dislocation nucleation process is disregarded.

The film is considered to be much thinner than the substrate and the strain relaxation by substrate bending is expected to be of minor relevance. Nevertheless, we include the induced curvature, since it will enable us to validate our results with substrate curvature measurements of a growing superlattice in potential follow-up studies.

In accordance with Euler-Bernoulli beam theory, see Fig. 1b, the relation between the normal strain $\varepsilon_x(z) = \varepsilon_y(z) = \overline{\varepsilon}(z)$, the radius of curvature ρ and the position of the axis with zero strain z_e can be written as

$$\overline{\varepsilon}(z) = \frac{z - z_e}{\rho}.$$
(2)

In order to estimate the two unknowns ρ and z_e , we define the force and moment equilibrium of the substrate-film system. We get:

$$\int_{-h_s}^0 \overline{M_s} \left(\frac{z - z_e}{\rho} \right) dz + \int_0^{h_f} \overline{M_f} \left(\frac{z - z_e}{\rho} + \varepsilon_m \right) dz = 0, \tag{3}$$

$$\int_{-h_{\rm s}}^{0} \overline{M_{\rm s}} \left(\frac{z - z_e}{\rho} \right) z \, \mathrm{d}z + \int_{0}^{h_{\rm f}} \overline{M_{\rm f}} \left(\frac{z - z_e}{\rho} + \varepsilon_{\rm m} \right) z \, \mathrm{d}z = 0, \tag{4}$$

for the force balance in *x*-direction and the moment balance with respect to the bending axis, respectively, for a system with unit thickness in *y*-direction. The mean strain ε_m due to the relaxed lattice mismatch depends on the lattice parameters of the substrate a_s and of the film a_f , the component of the Burgers vector parallel to the interface b_x and the misfit dislocation density:

$$\varepsilon_{\rm m} = \frac{a_{\rm s}[1 - \operatorname{sgn}\left(a_{\rm s} - a_{\rm f}\right)b_{\rm x}Q] - a_{\rm f}}{a_{\rm f}}.$$
(5)

 $\overline{M_s}$ and $\overline{M_f}$ denote the biaxial moduli of the substrate and the layer. For cubic crystal symmetry the biaxial modulus of a {001} plane is:

$$\overline{M} = c_{11} + c_{12} - \frac{2c_{12}^2}{c_{11}},\tag{6}$$

with

$$c_{11} = C_{iiii}, \quad c_{12} = C_{iijj}, \quad c_{44} = C_{ijij}, \quad i, j = 1, 2, 3.$$
 (7)

By substituting Eqs. 5 and 6 into Eqs. 3 and 4 the axis of zero strain and the curvature of the film-substrate system is determined as a



Fig. 1. (a) Three-dimensional unit cell of the film-substrate system with a network of orthogonal edge dislocation arrays, (b) Euler-Bernoulli beam theory model with deposition-induced curvature.

function of the misfit dislocation density *Q*. Considering the biaxial stress state, the strain energy per interface area is then evaluated by:

$$\frac{U_{\text{strain}}(\mathbf{Q})}{A} = \frac{1}{2} \int_{-h_s}^{0} 2\sigma_s \left(\frac{z-z_e}{\rho}\right) dz + \frac{1}{2} \int_{0}^{h_f} 2\sigma_f \left(\frac{z-z_e}{\rho} + \varepsilon_m\right) dz, \qquad (8)$$

with the biaxial stresses in the substrate and the film being:

$$\sigma_{\rm s} = \overline{M_{\rm s}} \left(\frac{z - z_e}{\rho} \right) \quad (-h_{\rm s} \le z \le 0), \tag{9}$$

$$\sigma_{\rm f} = \overline{M_{\rm f}} \left(\frac{z - z_e}{\rho} + \varepsilon_{\rm m} \right) \quad \left(0 \le z \le h_f \right). \tag{10}$$

Low dislocation densities justify the assumption of non-interacting dislocations within an array. It follows that the energy per interface area of parallel dislocations can be calculated by the line energy of a single dislocation multiplied by the misfit dislocation density. For taking into account the orthogonal dislocation arrays, this energy has to be doubled. The theory of linear elasticity breaks down in the region of the dislocation core with a radius r_c . Therefore, the dislocation line energy is divided into two parts, namely the nonelastic core energy per dislocation line length, $\frac{U_{core}}{L}$, and the linear elastic dislocation line energy outside the core, $\frac{U_{dislocle}}{L}$. Hence, Eq. 1 becomes:

$$\frac{U(Q)}{A} = \frac{U_{\text{strain}}(Q)}{A} + 2\left(\frac{U_{\text{disloc,le}}}{L} + \frac{U_{\text{core}}}{L}\right)Q.$$
(11)

For the sake of simplicity, the linear elastic part of the dislocation line energy is assessed by considering an infinite medium with elastic properties estimated by the arithmetic average of the adjacent constituents. According to Foreman [36] the elastic energy induced by a dislocation is:

$$\frac{U_{\text{disloc,le}}}{L} = \frac{Kb^2}{4\pi} \ln\left(\frac{R}{r_c}\right),\tag{12}$$

where K is the energy factor, being dependent on the material's anisotropy and the type of dislocation. For an edge dislocation in a cubic crystal K is given by

$$K = (c_{11} + c_{12}) \left[\frac{c_{44}(c_{11} - c_{12})}{c_{11}(c_{11} + c_{12} + 2c_{44})} \right]^{\frac{1}{2}}.$$
(13)

R represents the outer cut-off radius, which we set equal to the thickness of the deposited layer $h_{\rm f}$. It shall be mentioned that there exist various adaptions for the term $ln\left(\frac{h_{\rm f}}{r_{\rm c}}\right)$ in order to account for the free surface. Changing it to the often used term $ln\left(\frac{2h_{\rm f}}{r_{\rm c}}-\frac{1}{2}\right)$, e.g. [23],

does not significantly alter the resulting stress distribution in the superlattice and is therefore neglected. The dislocation core radius r_c is taken to be equal to the magnitude of the Burgers vector *b*. For transition metal nitrides the dislocation core line energy typically lies between 1 and 2 eV/Å, hence, the influence of $\frac{U_{core}}{L}$ within these boundaries is investigated. Even though the impact of the core energy is not negligible especially for small layer thicknesses, the qualitative behavior is rather unaffected.

The equilibrium configuration of the system is evaluated by minimizing Eq. 11 with respect to Q. A negative value of $(a_s - a_f)$ indicates that the lattice mismatch strain is reduced by removing a half plane of width b_x at a distance of $d = \frac{1}{0}$.

The energy contribution resulting from the interaction of the dislocations is not accounted for in the here presented approach — inevitably leading to an error in the evaluated misfit dislocation density. However, these contributions are expected to have a minor effect on the trends predicted for the crack growth resistance of a SL. Detailed studies on the energy of misfit dislocation arrays at a bimaterial interface including interaction energies can be found e.g. in [22,27,37–40].

2.2. Algorithm for the misfit dislocation density in a multilayer

A layerwise deposition of the superlattice is considered. Hence, the equilibrium state after each layer addition plays a decisive role for the formation of dislocations in the subsequent layers. Fig. 2 schematically depicts a superlattice with dislocations at the interfaces between two different transition metal nitrides with the direction of the Burgers vector parallel to the $\left[\overline{1}10\right]$ direction and a value of $b_j = b_{x,j} = a_j \frac{1}{\sqrt{2}}$. The alternating stress fields in a superlattice lead to misfit dislocations of opposite sign in consecutive layers.



Fig. 2. Schematic of the considered dislocation distribution in a superlattice of two different transition metal nitrides with Burgers vectors in the $[\overline{1}10]$ direction and dislocations of opposite sign in subsequently deposited layers. Both configurations, a perfectly sharp interface and a finite interface thickness with composition modulation, are studied.

The force and moment balances have to be fulfilled at each step of the layerwise assembling of the multilayer. Consequently, according to the superposition principle, the balances can be defined considering the change of forces and moments due to the *j*-th layer addition:

$$\int_{-h_{s}}^{0} \overline{M_{s}} \left(\frac{z - z_{e}^{(j)}}{\rho^{(j)}} \right) dz + \sum_{i=1}^{j-1} \int_{h_{i-1}}^{h_{i}} \overline{M_{i}} \left(\frac{z - z_{e}^{(j)}}{\rho^{(j)}} \right) dz + \int_{h_{j-1}}^{h_{j}} \overline{M_{j}} \left(\sum_{k=1}^{j} \frac{z - z_{e}^{(k)}}{\rho^{(k)}} + \varepsilon_{m,j} \right) dz = 0,$$
(14)

$$\int_{-h_{s}}^{0} \overline{M_{s}} \left(\frac{z - z_{e}^{(j)}}{\rho^{(j)}} \right) z \, dz + \sum_{i=1}^{j-1} \int_{h_{i-1}}^{h_{i}} \overline{M_{i}} \left(\frac{z - z_{e}^{(j)}}{\rho^{(j)}} \right) z \, dz$$

$$+ \int_{h_{j-1}}^{h_{j}} \overline{M_{j}} \left(\sum_{k=1}^{j} \frac{z - z_{e}^{(k)}}{\rho^{(k)}} + \varepsilon_{m,j} \right) z \, dz = 0.$$

$$(15)$$

Herein, the superscript (*j*) denotes the induced curvature/axis of zero strain due to the adding of the topmost layer and h_j denotes the distance between the substrate-film interface and the top of layer *j*, see Fig. 2, with $h_0 = 0$.

The mean misfit strain in the currently added layer is defined as

$$\varepsilon_{\mathrm{m},j} = \frac{\widehat{a}_{j-1} \left[1 - \mathrm{sgn}\left(\widehat{a}_{j-1} - a_j \right) b_{\mathrm{x},j} Q_j \right] - a_j}{a_j},\tag{16}$$

with \hat{a}_{j-1} being the lattice parameter of the previously deposited layer without curvature considering the formed dislocations:

$$\widehat{a}_{j-1} = \widehat{a}_{j-2} \left[1 - \operatorname{sgn} \left(\widehat{a}_{j-2} - a_{j-1} \right) b_{x,j-1} Q_{j-1} \right],$$
(17)

with $\hat{a}_0 = a_s$.

Similar to the deposition of a single layer, the axis of zero strain $z_e^{(j)}$ and the induced curvature $\rho^{(j)}$ can be calculated from Eq. 14 and Eq. 15 as a function of misfit dislocation density Q_j .

The strain state of the system after *j* layer depositions results from the superposition of the induced bending of all layers and the relaxed misfit strain:

$$\varepsilon_{\rm s}(z) = \sum_{k=1}^{j} \frac{z - z_e^{(k)}}{\rho^{(k)}} \quad (h_{\rm s} \le z \le 0), \tag{18}$$

$$\varepsilon_{i}(z) = \sum_{k=1}^{j} \frac{z - z_{e}^{(k)}}{\rho^{(k)}} + \varepsilon_{m,i} \quad (i = 1, \dots, n) \quad (h_{i-1} \le z \le h_{i}).$$
(19)

The biaxial stress state in the layers and the substrate after the deposition of n layers is:

$$\sigma_{\rm s}(z) = \overline{M_{\rm s}} \varepsilon_{\rm s}(z) \quad (h_{\rm s} \le z \le 0), \tag{20}$$

$$\sigma_i(z) = \overline{M_i} \varepsilon_i(z) \quad (i = 1, \dots n) \quad (h_{i-1} \le z \le h_i).$$
⁽²¹⁾

The strain energy per interface area as a function of the dislocation energy of the topmost layer is then given by:

$$\frac{U_{\text{strain}}(\mathbf{Q}_j)}{A} = \frac{1}{2} \int_{-h_s}^0 2\sigma_s \varepsilon_s dz + \frac{1}{2} \sum_{i=1}^j \int_{-h_{i-1}}^{h_i} 2\sigma_i \varepsilon_i dz.$$
(22)

The total energy becomes:

$$\frac{U(Q_j)}{A} = \frac{U_{\text{strain}}(Q_j)}{A} + 2\left(\frac{U_{\text{disloc,le}}}{L} + \frac{U_{\text{core}}}{L}\right)Q_j + \frac{U_{\text{disloc,prev}}}{A},$$
(23)

where $\frac{U_{\text{disloc,prev}}}{A}$ represents the dislocation line energy due to the dislocations formed in the previously deposited layers, not being a function of Q_j . Minimizing the total energy with respect to Q_j after each layer

deposition, we get the misfit dislocation density in all layers and, hence, the stress/strain distribution after *j* layer depositions.

The just described algorithm can be vastly simplified by neglecting the induced curvature and strain in the substrate, i.e. considering the substrate to be thick enough to be idealized as a half space. This reduces Eq. 22 to

$$\frac{J_{\text{strain}}^*(\mathbf{Q}_j)}{A} = \frac{1}{2} \sum_{i=1}^j \int_{h_{i-1}}^{h_i} 2\sigma_i \varepsilon_{\mathbf{m},i} dz,$$
(24)

with σ_i and $\varepsilon_{m, i}$ being constant between h_{i-1} and h_i and only the last summand depending on Q_j . The contribution to the total elastic energy per interface area $\frac{U^*(Q_j)}{A}$ being a function of Q_j is thus reduced to:

$$\frac{U^{*}(Q_{j})}{A} = (h_{j} - h_{j-1})\overline{M_{j}} \left\{ \frac{\hat{a}_{j-1} [1 - \operatorname{sgn}(\hat{a}_{j-1} - a_{j})b_{x,j}Q_{j}] - a_{j}}{a_{j}} \right\}^{2} + 2\left(\frac{U_{\text{disloc,le}}}{L} + \frac{U_{\text{core}}}{L}\right)Q_{j}.$$
(25)

By differentiating with respect to Q_j and solving for $\frac{\partial}{\partial Q_j} = 0$, we obtain the misfit dislocation density that minimizes the elastic energy per interface area. The misfit dislocation density Q_j can then be estimated by

$$Q_{j} = \frac{|a_{j} - \hat{a}_{j-1}|}{\hat{a}_{j-1}b_{x,j}} - \left(\frac{U_{\text{disloc,le}}}{L} + \frac{U_{\text{core}}}{L}\right) \frac{a_{j}^{2}}{M_{j}(h_{j} - h_{j-1})\hat{a}_{j-1}^{2}b_{x,j}^{2}},$$
(26)

with

$$\hat{a}_{j-1} = a_{\rm s} \prod_{n=1}^{j-1} [1 - \operatorname{sgn}(\hat{a}_{n-1} - a_n) b_{{\rm x},n} {\rm Q}_n].$$
⁽²⁷⁾

It should be noted that negative values resulting from Eq. 26 have to be set to zero and a negative or positive sign of $(a_j - \hat{a}_{j-1})$ indicates whether a half plane of $b_{x, j}$ is removed or added, respectively.

Perfectly sharp interfaces are often not achievable by physical vapor deposition. Therefore, additionally the effect of a finite interface thickness $h_{\text{interf}} = m\overline{a}$ is studied, with \overline{a} being the arithmetic mean value of the lattice parameter inherent to the adjacent layer materials and m being an integer number. The interface thickness is assumed to be independent of the bilayer period. A stepwise composition change is considered. Based on the interface thickness of m atomic layers, it is reasonable to define m + 1 composition steps. Dislocations are assumed to form at the *z*-position where the lattice misfit strain changes its sign, which is at the center of the interface for the studied configurations.

We intend to simulate the experimental evaluation of the fracture toughness of a superlattice performed on a micro-cantilever of freestanding film material. Information on the procedure and setup of a respective micromechanical experiment is given in [12] as well as in [41,42]. The substrate material is "removed" in the model and a new stress state, accounting for the force and moment balances of the freestanding film material, is determined. We want to emphasize, that within the presented model it is assumed that misfit dislocations form during the deposition process *only* and that the dislocation density cannot change thereafter. This results in a mere redistribution of the elastic strain within the film. The following assumptions are made at this point: The resulting stress state corresponds to a film entirely free of substrate material and, hence, slightly deviates from the actual boundary condition of a microcantilever, see Fig. 3. Furthermore, a pure bending stress distribution induced by the load *P* is assumed, neglecting the induced shear stresses.

2.3. Apparent fracture toughness

From the method discussed in section 2.2, an estimation for the residual stress state of the superlattice system after the entire deposition



Fig. 3. Schematic drawing of the considered micro-cantilever of free-standing film material. The detail depicts the configuration the weight function is applied to.

process is obtained. In this section, we aim to investigate the influence of the residual stress state on the crack growth resistance of the system. The stress intensity factor present in a cracked material is a superposition of the stress intensity due to external loading and the stress intensity due to the residual stress state. The contribution of the residual stresses is now considered as an alteration of the maximum bearable stress intensity of the system. The apparent fracture toughness K_{app} can be defined as:

$$K_{\rm app} = K_{\rm IC} - K_{\rm res},\tag{28}$$

with $K_{\rm IC}$ being the inherent Mode I critical stress intensity factor and $K_{\rm res}$ the stress intensity factor due to residual stresses.

The contribution of the residual stress state to the apparent fracture toughness is assessed by means of the weight function theory first proposed by Bueckner [34]. It allows to estimate the stress intensity factor as a function of crack length *a* for a given geometry with arbitrary stress distribution.

The stress intensity factor associated with the residual stress state $\sigma_{\rm res}$ is given by

$$K_{\rm res}(a) = \int_0^a h(z', a)\sigma_{\rm res}(z')dz',$$
(29)

where *z*' is the distance along the crack from the top surface and h(z',a) is the weight function. According to the setup of a pre-notched micro-cantilever fracture experiment, see [12], a weight function suitable for an edge cracked bar of thickness (*W*) derived by Fett [43] is applied:

$$h(z',a) = \sqrt{\frac{2}{\pi a}} \frac{1}{\sqrt{1 - \frac{z'}{a} \left(1 - \frac{a}{W}\right)^{\frac{3}{2}}}} \left[\left(1 - \frac{a}{W}\right)^{\frac{3}{2}} + \sum A_{\nu\mu} \left(1 - \frac{z'}{a}\right)^{\nu+1} \left(\frac{a}{W}\right)^{\mu} \right].$$
(30)

The values of the coefficients $A_{\nu\mu}$ are given in [43].

 Table 1

 Properties of the film and substrate materials

Material	c ₁₁ (GPa)	c ₁₂ (GPa)	c ₄₄ (GPa)	<u>₩</u> (GPa)	a (Å)	K _{IC} (MPa√m)	Ref.
TiN	575	130	163	646	4.25	2.05	[44,46]
CrN	516	115	116	580	4.14	1.84	[44,46]
MgO(100)	297	95	155	331	4.21	-	[47]



Fig. 4. Misfit dislocation density as a function of film thickness for a TiN and CrN single layer on MgO (100) for different core energies.

2.4. Sample superlattice configuration

Elastically anisotropic layer materials on an elastically anisotropic finite substrate are considered, all constituents having a face-centeredcubic structure. The elastic properties of the layer materials investigated within this study are extracted from Density Functional Theory studies [44,45] and summarized in Table 1. A (semi-)coherent interface between the MgO substrate and the first layer is assumed. The substrate thickness is defined to be 500 μ m for all calculations. If not stated otherwise, a perfectly sharp interface is considered. All sublayers are of equal thickness and the bilayer period is represented by Λ .

3. Results and discussion

3.1. Single layer misfit dislocation density

Fig. 4 shows the misfit dislocation densities evaluated for a TiN and CrN thin film single layer, respectively, on an MgO (100) substrate as a function of the film thickness $h_{\rm f}$. Considering $\frac{U_{\rm core}}{L} = 1.5 {\rm eV}/{\rm A}$, a critical thickness of ~1.2 nm for CrN and ~3.1 nm for TiN is determined. TiN, having a greater lattice parameter than MgO, is in a compressed state when deposited and will relax by a reduction of lattice planes. CrN, on the other hand, is under high tensile coherency stresses, which are reduced by introducing "extra" lattice planes within the film, when the thickness exceeds the critical thickness.

3.2. Multilayer misfit dislocation density

In the following, we discuss TiN/CrN superlattice films with equally thick TiN and CrN layers, but different bilayer periods $(h_{\text{TiN}} = h_{\text{CrN}} = \frac{\Lambda}{2})$ on MgO (100). Three different bilayer periods are chosen, two corresponding to a layer thickness $h_{l1} = 1.5$ nm $= \frac{\Lambda_l}{2}$ and $h_{l2} =$ 2.5 nm = $\frac{\Lambda_2}{2}$, where misfit dislocations are predicted for a monolithic CrN film, but not yet for a TiN film. Increasing the bilayer period to Λ_3 with $\frac{\Lambda_3}{2} = h_{13} = 5.0$ nm, dislocations are expected to form in all layers, regardless of the layer material. Both situations are studied, starting either with TiN or CrN, subsequently referred to as A/B = TiN/CrN (black curves) and A/B = CrN/TiN (green curves), respectively. Fig. 5a depicts the resulting misfit dislocation density in the individual layers for the three different architectures for both deposition sequences. For the smallest bilayer period $\Lambda_1 = 3$ nm no dislocations are predicted in the first layer for A/B = TiN/CrN. Hence, the TiN layer adapts to the lattice parameter of the MgO substrate resulting in a strain solely defined by the lattice misfit strain $\frac{a_{\rm MgO}-a_{\rm TIN}}{a_{\rm TIN}}$ and the induced curvature. For the



Fig. 5. (a) Misfit dislocation density, (b) resulting strained lattice parameter and (c) in-plane stresses in the individual layers for a superlattice composed of TiN and CrN layers on MgO (100) with three different bilayer periods.

subsequently deposited CrN layer a misfit dislocation density of $Q \approx 6.5 \times 10^4 {\rm cm}^{-1}$ is energetically favoured. This results in a slight change of the mean lattice parameter towards that of stress-free CrN, see Fig. 5b. Even though this induces a higher misfit strain in the next TiN layer, energy minimization after each time a new layer is added, predicts a rather constant lattice parameter, due to the absence of dislocations in the rest of the film. Consequently, the magnitude of in-plane compressive stress in the TiN layers is increased compared to that of a dislocation-free single layer $\sigma_{0,TIN}$, whereas the tensile stress in CrN layers is decreased compared to $\sigma_{0,CrN}$ (Fig. 5c). Changing the sequence of layer deposition, i.e. starting with CrN, dislocations are formed in the first layer, whereas the rest is predicted to be dislocation-free. The resulting mean lattice parameter and, thus, stress state coincide with the values determined for the TiN/CrN sequence.

When increasing the bilayer period to $\Lambda = 5$ nm, the formation of dislocations starts again in the first CrN layer, but now alters the mean lattice parameter to an extent high enough to induce misfit dislocations in the TiN layers. The resulting misfit dislocation density is quite similar for both layer materials, being 18.3×10^4 cm⁻¹ for TiN layers and 18.7×10^4 cm⁻¹ for CrN layers. The plot in the middle of Fig. 5c indicates that the magnitude of compressive stresses is still higher compared to the mismatch-stresses of a dislocation-free superlattice.

A bilayer period of 10 nm provokes misfit dislocations in the first layer, independent of the starting layer material. A misfit dislocation density of 46.5×10^4 cm⁻¹ and 47.1×10^4 cm⁻¹ for TiN and CrN, respectively, is estimated for both sequences. The stresses are reduced in each sublayer with respect to the dislocation-free thin film.

For all three architectures, the model predicts that the stress state in the first bilayer slightly deviates from the rather constant stress amplitudes in the rest of the multilayer film. Fig. 6a exemplarily depicts the stress state of the top four layers of a TiN/CrN superlattice deposited on MgO with $\Lambda = 5$ nm and a total film thickness of $h_f = 1.5$ µm. The blue curves correspond to a superlattice film with perfectly sharp interfaces, while the stress distribution in a superlattice film with at finite

interface thickness (here $h_{\text{interf}} = 2\overline{a} \approx 8.4\text{A}$) is shown in red. The dots indicate the magnitude of stress considered in Fig. 6b, which presents the bilayer-period-dependency of the stress state. It should be noted that the stress state of both layers is represented by a positive value. The actual type of stresses, compressive or tensile, is indicated within the legend.

For very small bilayer periods, the stress state in both superlattice constituents correspond to their lattice mismatch with respect to MgO (see identical in-plane stress values of solid and dashed lines in Fig. 6b). Considering a perfectly sharp interface and increasing the bilayer period to $\Lambda \sim 2.5$ nm, dislocations start to form in the CrN layers resulting in a relaxation of tensile stresses (continuous dark blue curve), whereas the compressive stresses in TiN layers (continuous light blue curve) increase until dislocations are introduced within TiN layers as well at $\Lambda \sim 3.6$ nm. Accordingly, the curve of compressive stresses shows an increase and subsequent decrease with its peak at $\Lambda \sim 3.6$ nm.

The results for the bilayer-period-dependency of the stress state with and without finite interface thickness cannot be compared quantitatively, since the stress state within the interfaces is not captured by the values plotted in Fig. 6b. However, it can be deduced that a thicker interface shifts the peak of compressive stresses to higher bilayer periods. This is because dislocations start to form at an increased layer thickness compared to the perfectly sharp interface configuration since part of the layer thickness is occupied by the interface with a lower inherent lattice mismatch.

As mentioned in section 2, evaluating the apparent fracture toughness according to the experimental setup requires modelling free-standing film material. Removing the substrate induces a stress redistribution within the layers in such a way that, due to the equilibrium conditions, the resulting compressive stresses in TiN are of quite the same magnitude as tensile stresses in CrN for all bilayer periods, see dashed/dotted lines in Fig. 6. Hence, the observed peak in compressive stresses is not perceivable anymore after removing the substrate. It



Fig. 6. (a) Stress distribution in the top layers of a TiN/CrN superlattice deposited on MgO with total thickness $W = 1.5 \mu m$ and $\Lambda = 5 nm$ considering either a perfectly sharp interface or an interface thickness of $h_{interf} = 2\overline{a}$ with stepwise composition modulation. The dots in (a) indicate the stress values used to represent the bilayer-period-dependent compressive and tensile stresses in (b), exemplary plotted for $\Lambda = 5 nm$. In (b) a comparison between the in-plane stresses present in the superlattice after deposition (attached to the substrate) and after removing the substrate is provided. The dashed line shows the stresses of a fictious scenario of suppressed dislocation formation.

should be noted that the residual stresses induced by a temperature change resulting from a mismatch of coefficients of thermal expansion (CTE) are neglected for the considered material combination. In [48] the CTEs of TiN and CrN as a function of temperature are investigated, demonstrating comparable behavior and magnitude. Thus, cooling down from deposition to room temperature results in stresses about one magnitude smaller than the lattice mismatch related stresses and do not show a bilayer-period-dependency.

3.3. Apparent fracture toughness of multilayers

For studying the apparent fracture toughness, it should be recalled, that the coordinate system is changed such that its origin is positioned at the free surface of the top layer (corresponding to the right side of Fig. 6a). Taking into account the stress distribution depicted by dashed/ dotted lines in Fig. 6a and applying Eq. 29 with the appropriate weight function, we obtain the stress intensity factor resulting from the residual stress state. As discussed in several studies [49–52], the crack growth resistance of a multilayer is not only influenced by its stress state but also by the spatial variation of elastic properties of the constituents. However, the influence of the latter is expected to be negligibly small for the considered superlattices, since the constituents are of the same material family with biaxial moduli differing by approximately 10%.

Fig. 7 visualizes the spatially varying inherent fracture toughness K_{IC} (green curves), the stress intensity factor associated with the residual



Fig. 7. Alteration of the apparent fracture toughness in the top few layers of an SL with $\Lambda = 5nm$ resulting from the spatially varying inherent fracture toughness and the stress intensity factor associated with the residual stress state. Top and bottom panels correspond to perfectly sharp interfaces and interface thicknesses of $h_{\text{interf}} = 2\overline{a}$, respectively.

stress state K_{res} (blue, red curves) and the consequent alteration of K_{app} (black curves) as a function of the ratio between crack length and cantilever thickness, a/W. The top three bilayers are depicted. We see that the inherently lower fracture toughness of CrN is further reduced by its tensile stresses, whereas compressive stresses in TiN layers enhance the maximum bearable stress intensity. Consistent with the other material properties, we consider a stepwise modulation of K_{IC} over the interface thickness (Fig. 7b). Despite the higher stresses within the layers when considering an interface thickness of $h_{\text{interf}} = 2\overline{a}$ (see the slightly higher peak of the light red curve compared to the light blue curve in Fig. 6), there is no significant difference in maximum apparent fracture toughness. This stems from the fact that the layer thickness being subject to these high stresses is reduced by the interface thickness.

Fig. 8 illustrates the behavior of K_{app} for a superlattice with $\Lambda = 5 \text{ nm}$ as a function of a/W up to a crack length relevant for fracture toughness experiments on micro-cantilevers. It shows that the maxima, appearing when the crack tip has just penetrated an entire TiN layer, do not vary significantly between consecutive bilayers. Furthermore, it should be noted that one of these maxima will always be reached. A crack with its tip lying within a tensile (CrN-) layer will demonstrate unstable crack growth until reaching a compressive layer. Then stable crack growth will occur until reaching the next local maximum.

An initial crack length of $a/W \approx 0.3$ is defined and the maximum value of the apparent fracture toughness within the adjacent layers is considered as the system's apparent fracture toughness K_{app}^* . Presenting this value as a function of the bilayer period, see Fig. 9, clearly demonstrates an enhancement of K_{app}^* with respect to the inherent fracture toughness of the superlattice's constituents. Moreover, an initial steep rise and more gentle decrease of K_{app}^* is predicted. For low bilayer



Fig. 8. Apparent fracture toughness as a function of the ratio between crack length and cantilever thickness a/W for $\Lambda = 5 \text{ nm}$. $K^*_{\text{app,0.3}}$ indicates the considered apparent fracture toughness estimated for an initial crack length of $a/W \approx 0.3$.

periods, the system's apparent fracture toughness follows the anticipated curve of a system with suppressed dislocation formation. This fictious scenario corresponds to a stress state barely depending on the bilayer period (merely substrate bending alters the stresses to a negligibly small extent). Hence, the constant increase of K_{app}^* solely stems from the change of individual layer thickness contributing to K_{res} . Even though dislocations in CrN start forming at a smaller bilayer period, the curves match up to $\Lambda \approx 3.6$ nm, i.e. the critical bilayer period for the formation of dislocations in TiN. This is because the equilibrium stress state after removing the substrate remains rather unchanged until reaching a bilayer period where dislocations are formed in both layer materials, compare Fig. 6b. Similar to the bilayer-perioddependent stress state, also the peak in K_{app}^* is shifted to higher bilayer periods and reaches a slightly higher maximum when considering an interface thickness of $h = 2\overline{a}$. It should be noted that for higher bilayer periods the misfit dislocation density might be underestimated in the present model. With decreasing distance between the dislocations within an array, the interaction of their stress fields becomes more relevant. The reduced dislocation self-energy, discussed e.g. by Atkinson et al. [23], allows for higher dislocation densities and, hence, further decreases the coherency stresses. However, the range of bilayer periods at



Fig. 9. System's apparent fracture toughness estimated for $a/W \approx 0.3$ as a function of bilayer period for a superlattice with perfectly sharp interface (blue line) and with a finite interface thickness (red line). The dotted line depicts the constant increase of K_{app}^* if no misfit dislocations were considered.

which we predict the pronounced fracture toughness enhancement, is not affected due to rather low dislocation densities.

Decreasing the minimum bilayer period to very low values (lower values than shown in Fig. 9), presumably would lead to a loss of the layer structure (cf. Refs. [7, 8]). The fracture toughness of the resulting "solid solution" is expected to follow the rule of mixture (hence, further reduction of K_{app}^* with decreasing bilayer period).

4. Summary and conclusions

Encouraged by the fracture toughness enhancement experimentally observed in superlattice coatings, a continuum mechanics based model with the main objective to elucidate the underlying mechanisms was developed. By minimizing the overall elastic energy of the substrate/ film system each time a new layer is added onto the multilayer stack, misfit dislocation densities as well as evolving coherency stresses were determined for different architectures of TiN/CrN SLs. The resulting alternating compressive/tensile stresses in the layers exhibit a strong bilayer-period-dependency, whereby the predicted increase in compressive stresses for small bilayer periods is attributed to the higher critical thickness of TiN compared to CrN deposited on a MgO substrate. To allow for comparison with fracture toughness experiments performed on free-standing film material, the substrate was removed after the aforementioned simulation procedure. In contrast to monolithic films, where removing the substrate results in a stress-free state, the stresses in a superlattice are just redistributed within the film. However, the pronounced peak in compressive stresses is no longer observable. In a final step, the weight function method was applied to link the predicted stress profiles with the crack growth resistance. We found higher critical stress intensity values for all SLs in comparison with the intrinsic fracture toughness of the constituent layer, see Fig. 10 (solid line). The crack growth resistance increases with increasing bilayer period for dislocation-free (very thin) SLs (region 2). First dislocations forming in one SL constituent reduce stresses in the corresponding layer material, whereas the strain in the other constituent is increased. However, finding a new equilibrium after removing the substrate results in stresses similar to the dislocation-free configurations, leading to a further increase in apparent fracture toughness (region 3). Only



Fig. 10. Schematic illustration of the different mechanisms influencing the apparent fracture toughness of a TiN/CrN superlattice. The dotted line represents the expected behavior for very low bilayer periods resulting in a "solid solution".

when a critical layer thickness is exceeded and formation of misfit dislocations becomes energetically favorable in both SL constituents, the fracture toughness values decrease again (region 4). In [12] the apparent fracture toughness values obtained by applying the presented model to a TiN/Cr_{0.37}AlN_{0.63} superlattice perfectly matched experimental results for bilayer periods between 2.5 and 22.0 nm. The excellent agreement suggests that the model is able to capture the most relevant mechanisms responsible for the experimentally observed bilayerperiod-dependent fracture toughness. What is more, the proposed method can be easily applied to different material systems in order to predict the most promising bilayer period for enhancing the apparent fracture toughness. To exploit the superlattice effect in fracture toughness to its maximum potential, the influence of the relevant parameters, i.e. lattice and elastic mismatch, interface width, bilayer period and inherent fracture toughness of the constituents, may be investigated in a parametric study.

Data availability

The raw/processed data required to reproduce these findings cannot be shared at this time due to technical or time limitations.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgement

The authors highly acknowledge the financial support of the Austrian Science Fund (FWF): P30341-N36.

References

- G. Greczynski, J. Patscheider, J. Lu, B. Alling, A. Ektarawong, J. Jensen, I. Petrov, J.E. Greene, L. Hultman, Control of Ti1-xSixN nanostructure via tunable metal-ion momentum transfer during HIPIMS/DCMS co-deposition, Surf. Coatings Technol. 280 (2015) 174–184, https://doi.org/10.1016/j.surfcoat.2015.09.001.
- [2] F. Fernandes, S. Calderon, P.J. Ferreira, A. Cavaleiro, J.C. Oliveira, Low peak power deposition regime in HiPIMS: Deposition of hard and dense nanocomposite Ti-Si-N films by DOMS without the need of energetic bombardment, Surf. Coatings Technol. 397 (2020) 125996, https://doi.org/10.1016/j.surfcoat.2020.125996.
- [3] R. Daniel, M. Meindlhumer, W. Baumegger, J. Zalesak, B. Sartory, M. Burghammer, C. Mitterer, J. Keckes, Grain boundary design of thin films: Using tilted brittle interfaces for multiple crack deflection toughening, Acta Mater. 122 (2017) 130–137, URL https://doi.org/10.1016/j.actamat.2016.09.027.
- [4] H. Kindlund, D.G. Sangiovanni, I. Petrov, J.E. Greene, L. Hultman, A review of the intrinsic ductility and toughness of hard transition-metal nitride alloy thin films, Thin Solid Films 688 (2019) 137479, https://doi.org/10.1016/j.tsf.2019.137479.
- [5] R. Daniel, M. Meindlhumer, J. Zalesak, W. Baumegger, J. Todt, T. Ziegelwanger, J.F. Keckes, C. Mitterer, J. Keckes, Multi-scale interface design of strong and damage resistant hierarchical nanostructured materials, Mater. Des. 196 (2020) 109169, https://doi.org/10.1016/j.matdes.2020.109169.
- [6] L. Hultman, Synthesis, structure, and properties of superhard superlattice coatings, Nanostructured Coatings, Nanostructure Science and Technology, 1 ed.Springer 2006, pp. 539–554, https://doi.org/10.1007/978-0-387-48756-4_13.
- [7] U. Helmersson, S. Todorova, S.A. Barnett, J.E. Sundgren, L.C. Markert, J.E. Greene, Growth of single-crystal TiN/VN strained-layer superlattices with extremely high mechanical hardness, J. Appl. Phys. 62 (1987) 481–484, https://doi.org/10.1063/1. 339770.
- [8] X. Chu, S.A. Barnett, Model of superlattice yield stress and hardness enhancements, J. Appl. Phys. 77 (1995) 4403–4411, https://doi.org/10.1063/1.359467.
- [9] R. Hahn, M. Bartosik, R. Soler, C. Kirchlechner, G. Dehm, P.H. Mayrhofer, Superlattice effect for enhanced fracture toughness of hard coatings, Scr. Mater. 124 (2016) 67–70, https://doi.org/10.1016/j.scriptamat.2016.06.030.
- [10] J. Buchinger, N. Koutná, Z. Chen, Z.L. Zhang, P.H. Mayrhofer, D. Holec, M. Bartosik, Toughness enhancement in TiN/WN superlattice thin films, Acta Mater. 172 (2019) 18–29, https://doi.org/10.1016/j.actamat.2019.04.028.
- R.O. Ritchie, The conflicts between strength and toughness, Nat. Mater. 10 (2011) 817–822, https://doi.org/10.1038/nmat3115.
- [12] J. Buchinger, A. Wagner, Z. Chen, Z. Zhang, D. Holec, P. Mayrhofer, M. Bartosik, Fracture toughness trends of modulus-matched TiN/(Cr,Al)N thin film superlattices, Acta Mater. 202 (2020) 376–386, https://doi.org/10.1016/j.actamat.2020.10.068.
- [13] R. Hahn, N. Koutná, T. Wójcik, A. Davydok, S. Kolozsvári, C. Krywka, D. Holec, M. Bartosik, P.H. Mayrhofer, Mechanistic study of superlattice-enabled high toughness

and hardness in MoN/TaN coatings, Commun. Mater. 1 (2020)https://doi.org/10. 1038/s43246-020-00064-4.

- [14] J. Buchinger, N. Koutná, Z. Chen, Z.L. Zhang, P.H. Mayrhofer, D. Holec, M. Bartosik, Toughness enhancement in TiN/WN superlattice thin films, Acta Mater. 172 (2019) 18–29, https://doi.org/10.1016/j.actamat.2019.04.028.
- [15] P. Řehák, M. Černý, D. Holec, Interface-induced electronic structure toughening of nitride superlattices, Surf. Coatings Technol. 325 (2017) 410–416, https://doi.org/ 10.1016/j.surfcoat.2017.06.065.
- [16] Z. Zhang, X. Gu, D. Holec, M. Bartosik, P.H. Mayrhofer, H.P. Duan, Superlatticeinduced oscillations of interplanar distances and strain effects in the CrN/AlN system, Phys. Rev. B 95 (2017) 1–7, https://doi.org/10.1103/PhysRevB.95.155305.
- [17] LB. Freund, S. Suresh, Thin Film Materials: Stress, Defect Formation and Surface Evolution, Cambridge University Press, 2004 https://books.google.at/books?id= 9UNnzNYAkboC.
- [18] F.C. Frank, J.H. Van Der Merwe, One-dimensional dislocations. II. Misfitting monolayers and oriented overgrowth, Proc. R. Soc. A Math. Phys. Eng. Sci. (1949) 216–225, https://doi.org/10.1098/rspa.1949.0096.
- [19] J.H. Van Der Merwe, Crystal interfaces. Part I. Semi-infinite crystals, J. Appl. Phys. 34 (1963) 117–122, https://doi.org/10.1063/1.1729050.
- [20] J.H. Van Der Merwe, Equilibrium structure of a thin epitaxial film, J. Appl. Phys. 41 (1970) 4725–4731, https://doi.org/10.1063/1.1658522.
- [21] J.W. Matthews, A.E. Blakeslee, Defects in epitaxial multilayers: I. misfit dislocations, J. Cryst. Growth 27 (1974) 118–125, https://doi.org/10.1016/S0022-0248(74) 80055-2.
- [22] J.R. Willis, S.C. Jain, R. Bullough, The energy of an array of dislocations: implications for strain relaxation in semiconductor heterostructures, Philos. Mag. A 62 (1990) 115–129, https://doi.org/10.1080/01418619008244339.
- [23] A. Atkinson, S.C. Jain, The energy of finite systems of misfit dislocations in epitaxial strained layers, J. Appl. Phys. 72 (1992) 2242–2248, https://doi.org/10.1063/1. 351617.
- [24] D. Holec, P.M. Costa, M.J. Kappers, C.J. Humphreys, Critical thickness calculations for InGaN/GaN, J. Cryst. Growth 303 (2007) 314–317 https://www.sciencedirect.com/ science/article/pii/S002202480601623X#bib5 https://doi.org/10.1016/j.jcrysgro. 2006.12.054.
- [25] D. Andersen, R. Hull, Effect of asymmetric strain relaxation on dislocation relaxation processes in heteroepitaxial semiconductors, J. Appl. Phys. 121 (2017) 075302, https://doi.org/10.1063/1.4975789.
- [26] M.Y. Gutkin, A.L. Kolesnikova, A.E. Romanov, Misfit dislocations and other defects in thin films, Mater. Sci. Eng. A 164 (1993) 433–437, https://doi.org/10.1016/0921-5093(93)90707-L.
- [27] M.Y. Gutkin, K.N. Mikaelyan, I.A. Ovid'ko, Equilibrium configurations of partial misfit dislocations in thin-film heterosystems, Phys. Solid State 40 (1998) 1864–1869, https://doi.org/10.1134/1.1130674.
- [28] R.H.M. Van De Leur, A.J.G. Schellingerhout, F. Tuinstra, J.E. Mooij, Critical thickness for pseudomorphic growth of Si/Ge alloys and superlattices, J. Appl. Phys. 64 (1988) 3043–3050, https://doi.org/10.1063/1.341568.
- [29] J.P. Hirth, X. Feng, Critical layer thickness for misfit dislocation stability in multilayer structures, J. Appl. Phys. 67 (1990) 3343–3349, https://doi.org/10.1063/1.345371.
- [30] A.J. Blattner, R. Lakshminarayanan, D.K. Shetty, Toughening of layered ceramic composites with residual surface compression: effects of layer thickness, Eng. Fract. Mech. 68 (2001) 1–7, https://doi.org/10.1016/S0013-7944(00)00096-5.
- [31] R.J. Moon, M. Hoffman, J. Hilden, K. Bowman, K. Trumble, J. Rödel, Weight function analysis on the R-curve behavior of multilayered alumina-zirconia composites, J. Am. Ceram. Soc. 85 (2002) 1505–1511, https://doi.org/10.1111/j.1151-2916.2002. tb00304.x.
- [32] M. Lugovy, V. Slyunyayev, N. Orlovskaya, G. Blugan, J. Kuebler, M. Lewis, Apparent fracture toughness of Si3N4-based laminates with residual compressive or tensile stresses in surface layers, Acta Mater. 53 (2005) 289–296, https://doi.org/10.1016/ j.actamat.2004.09.022.
- [33] C.R. Chen, J. Pascual, F.D. Fischer, O. Kolednik, R. Danzer, Prediction of the fracture toughness of a ceramic multilayer composite - modeling and experiments, Acta Mater. 55 (2007) 409–421, https://doi.org/10.1016/j.actamat.2006.07.046.
- [34] H.F. Bueckner, Novel Principle for the Computation of Stress Intensity Factors, Zeitschrift fuer Angew, Math. Mech. 50 (1970) 529–546, URL https://trid.trb.org/ view.aspx?id=3976.
- [35] L. Hultman, M. Shinn, P.B. Mirkarimi, S.A. Barnett, Characterization of misfit dislocations in epitaxial (001)-oriented TiN, NbN, VN, and (Ti,Nb) N film heterostructures by transmission electron microscopy, J. Cryst. Growth 135 (1994) 309–317, https:// doi.org/10.1016/0022-0248(94)90757-9.
- [36] A.J.E. Foreman, Dislocation energies in anisotropic crystals, Acta Metall. 3 (1955) 322–330, https://doi.org/10.1016/0001-6160(55)90036-5.
- [37] A. Rockett, C.J. Kiely, Energetics of misfit-and threading- dislocation arrays in heteroepitaxial films, Phys. Rev. B 44 (1991) 1154–1162.
- [38] A.J. Vattré, M.J. Demkowicz, Determining the burgers vectors and elastic strain energies of interface dislocation arrays using anisotropic elasticity theory, Acta Mater. 61 (2013) 5172–5187, https://doi.org/10.1016/j.actamat.2013.05.006.
- [39] A. Vattré, Mechanical interactions between semicoherent heterophase interfaces and free surfaces in crystalline bilayers, Acta Mater. 93 (2015) 46–59, https://doi. org/10.1016/j.actamat.2015.04.007.
- [40] A. Vattré, Elastic interactions between interface dislocations and internal stresses in finite-thickness nanolayered materials, Acta Mater. 114 (2016) 184–197, https:// doi.org/10.1016/j.actamat.2016.04.044.
- [41] G. Dehm, B. Jaya, R. Raghavan, C. Kirchlechner, Overview on micro- and nanomechanical testing: New insights in interface plasticity and fracture at small length scales, Acta Mater. 142 (2018) 248–282, https://doi.org/10.1016/j.actamat.2017. 06 019

- [42] J. Ast, M. Ghidelli, K. Durst, M. Göken, M. Sebastiani, A.M. Korsunsky, A review of experimental approaches to fracture toughness evaluation at the micro-scale, Mater. Des. 173 (2019) 107762, https://doi.org/10.1016/j.matdes.2019.107762.
- [43] T. Fett, Stress intensity factors and weight functions for the edge cracked plate calculated by the boundary collocation method, technical report, Kernforschungszentrum Karlsruhe (1990) https://doi.org/10.1063/1.3022907.
- [44] D. Holec, M. Friák, J. Neugebauer, P.H. Mayrhofer, Trends in the elastic response of binary early transition metal nitrides, Phys. Rev. B - Condens. Matter Mater. Phys. 85 (2012) https://doi.org/10.1103/PhysRevB.85.064101.
- [45] L. Zhou, D. Holec, P.H. Mayrhofer, First-principles study of elastic properties of cubic Cr 1-xAlxN alloys, J. Appl. Phys. 113 (2013), 043511, https://doi.org/10.1063/1. 4789378.
- [46] L. Löfler, P. H. Mayrhofer, M. Bartosik, D. Holec, Mechanical properties of CrN-based superlattices, to be Submitt. (2021).
- [47] C.S. Zha, H.K. Mao, R.J. Hemley, Elasticity of MgO and a primary pressure to 55 GPa, Proc. Natl. Acad. Sci. U. S. A. 97 (2000) 13494–13499, https://doi.org/10.1073/pnas. 240466697.

- [48] M. Bartosik, D. Holec, D. Apel, M. Klaus, C. Genzel, J. Keckes, M. Arndt, P. Polcik, C.M. Koller, P.H. Mayrhofer, Thermal expansion of Ti-Al-N and Cr-Al-N coatings, Scr. Mater. 127 (2017) 182–185, https://doi.org/10.1016/j.scriptamat. 2016.09.022.
- [49] H. Gao, Fracture analysis of nonhomogeneous materials via a moduli-perturbation approach, Int. J. Solids Struct. 27 (1991) 1663–1682, https://doi.org/10.1016/0020-7683(91)90068-Q.
- [50] S. Muju, Crack propogation in bimaterial multilayered periodically microcracking composite media, Compos. Sci. Technol. 60 (2000) 2213–2221, https://doi.org/10. 1016/S0266-3538(00)00016-6.
- [51] O. Kolednik, J. Predan, G.X. Shan, N.K. Simha, F.D. Fischer, On the fracture behavior of inhomogeneous materials - a case study for elastically inhomogeneous bimaterials, Int. J. Solids Struct. 42 (2005) 605–620, https://doi.org/10.1016/j.ijsolstr.2004. 06.064.
- [52] O. Kolednik, J. Predan, F.D. Fischer, P. Fratzl, Improvements of strength and fracture resistance by spatial material property variations, Acta Mater. 68 (2014) 279–294, https://doi.org/10.1016/J.ACTAMAT.2014.01.034.