

Influence of nitrogen on the design and mechanical properties of multilayered metal nitride coatings

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Abstract:

This work proposes two distinct methods to characterise mechanically and structurally $\text{Ti}_{0.54}\text{Al}_{0.46}\text{N}/\text{Ti}_{0.67}\text{Al}_{0.33}$ multilayer coatings, referred to as TiAlN/TiAl respectively deposited by reactive gas pulsing process. In the first method, the properties of the coating are supposed to be driven by the volume fraction of TiAlN (V_f). To directly quantify this volume fraction from mechanical response, an analytical model and a finite element model representing an equivalent homogenized multilayered coating were calibrated. Similar results are found for both models: an imbalance between TiAl and TiAlN lead to an increase of V_f with the decrease of the period Λ . The second method consists of evaluating the mechanical properties of the interface between adjacent layers through density functional theory and molecular dynamics calculations. The results indicate that the interfaces exhibit a higher hardness and elastic modulus than predicted by a rule of mixtures. This enhancement is attributed to the presence of nitrogen within the transition layer. A very good correlation is observed between V_f and $1/\Lambda$ suggesting that the mechanical properties of any multilayer with a particular period value can be extrapolated.

Keywords: ab initio calculations; finite elements; nanoindentation; multilayered coatings; interfaces

1 Introduction

Widely present in industry since the late 1980s, multilayer coatings have been used as high-performance protective coatings, particularly for cutting tools. It has been shown that the alternation of a ductile and a rigid material in such coating allows to enhance their mechanical properties [1,2]. The mechanical properties of these coatings greatly depend on the stacking

period: generally, the lower the period is, the better the mechanical properties are. Misra et al. [3] have shown that Cu/Nb multilayers exhibit very different hardness depending on the period, while conserving a similar indentation modulus. Based on the Hall-Petch effect [4], they have elaborated a model accounting for the confined plasticity due to the interface existing between the different layers. This hardness enhancement can also be accompanied by a toughness increase [5–10]. For some case the indentation elastic modulus may be also affected as well [11] suggesting that the interface between the two layers doesn't play only the role of dislocation barriers. In this way, interface cannot be longer considered as a 2-dimensionnal surface frontier but becomes a 3-dimensional region with its own thickness and properties. The influence of this interface, generally with a nanometric thickness, on the properties of the whole multilayer becomes predominant as the stacking period reaches nanometric values. Today, the mechanical but also the structural characterisation of such nanometric interface layer becomes critical [12].

For a nanometric period, the interfaces are too thin to be characterised mechanically using experimental means. Recently, Giljean et al. [13] have proposed to evaluate the thickness of the interface layer by calibrating a finite element model of indentation experimental curves obtained on multilayers with different stacking periods. However, this method requires strong assumptions about the mechanical behaviour law used for the interface layer and strong calculation means due to the fineness of the microstructure. In this work, a different approach is proposed. As Giljean et al., we propose a model calibration based on indentation curves, but using an equivalent homogeneous coating model constituted of the two constituents (TiAl and TiAlN) of the multilayer coating and adjusting a volumetric fraction of them.

DFT (Density Functional Theory) calculations appear as another option to assess to both microstructural and mechanical properties of these very thin interface layers [14,15]. Recently, using such type of calculations, Zhang et al. [12] have studied the mechanical response of different type of interfaces dedicated to multilayer structures. However, their study focuses on perfect interfaces with sharp transition between the different layers. In particular, the case for which a possible third material is formed between the two layers is not envisaged while such calculations methods would allow it. In fact, by forming a super structure by stacking two layers and then relaxing it by MD (molecular dynamics) calculations [16] to stabilise them thermodynamically, it becomes possible to recreate an interface between two layers of the coating. Such structures can then be characterised mechanically using semi-empirical methods [17–23]. Here DFT calculations are performed to predict the structure and the mechanical properties of the two constituents of the multilayers (TiAl and TiAlN). The structures are optimised based on their Knoop hardness.

This work is organized as follows. Section 2 outlines materials and methods used during this work, beginning with a description of the deposition methods of the studied samples and their characteristics in section 2.1. Then details about the X-ray diffraction (XRD) characterisation of these samples are given in section 2.2. Then details about Electron Energy Loss Spectroscopy (EELS) and Transmission Electron Microscopy (TEM) characterizations are given in section 2.3. Then mechanical characterisation of the samples by nanoindentation and a description of the indentation FEM Finite Element Model (FEM) used to determine their mechanical properties with Finite Element Model Updating (FEMU) method are given section 2.4. The ab-initio calculations methods are detailed, notably the method for the determination of the Knoop hardness alongside the one of the material properties from the elastic tensor thanks to Voigt, Reuss and Hill method and the Vickers Hardness one with Oganov et al. model in section 2.5. Finally, a description of the

interface's characteristics and the molecular dynamics calculations conditions, are shown in section 2.6. Section 3 describes the different results obtained in this work and a discussion regarding them. First, the results related to micro and nanostructural characterisation such as XRD, TEM and EELS are presented in section 3.1. Then, nanoindentation, including the indentations curve of the samples, are presented in section 3.2. These results are followed in section 3.3 by the ones obtained with the homogenised model. Afterward, the results related to the DFT calculations of the TiAl and TiAlN structures are presented in section 3.4. Finally, the results of the molecular dynamics are shown in section 3.5. These results include the interfaces relaxation internal energy evolution, the displacements of the different atoms over time and the comparison between the mechanical properties of the isolated interfaces with the tailored material with equal proportions of TiAlN and TiAl. The conclusion section summarises all the results obtained.

2 Material and methods

2.1 Monolithic and multilayer coatings deposition

The monolithic and multilayer coatings were deposited in an Alliance Concept AC450 vacuum reactor, by radiofrequency magnetron cathodic sputtering using the Reactive Gas Pulsing Process (RGPP) [24]. This is a vacuum deposition technique for sputtering a TiAl sintered metallic target (ratio Ti/Al = 2) and deposit metal or metallic nitride onto (100) silicon substrate by pulsing periodically and control a flow of nitrogen inside the chamber. It is then possible to modulate the $\text{Ti}_{0.67}\text{Al}_{0.33}/\text{Ti}_{0.54}\text{Al}_{0.46}\text{N}$ stacking of the multilayer coating at the nanometer scale. In this work, we focused on $\text{Ti}_{0.67}\text{Al}_{0.33}$ alloy and the corresponding $\text{Ti}_{0.54}\text{Al}_{0.46}\text{N}$ nitride (referred to as TiAlN and TiAl, respectively) because with a 50% at. of Al content, the nitride exhibits the highest mechanical properties [25].

The deposition parameters are set based on sputtering yield of the components to have an expected equal thickness of TiAlN and TiAl nanolayers. The depositions have been made at a sputtering frequency of 13.56 MHz, at room temperature in an Ar or Ar+N₂ atmosphere with an argon partial pressure of 0.52 Pa. The distance between the target and the substrate was fixed at 60 mm, and a sputtering power of 80 W was applied. A 45 nm $\text{Ti}_{0.67}\text{Al}_{0.33}$ buffer layer was systematically deposited on the etched substrates to enhance film adhesion. All deposits were realised with a constant pumping speed of 10 l.s⁻¹ and a constant argon flow rate of 3 sccm (standard cubic centimetre per minute). In the case of monolithic coatings, the nitrogen flow is controlled using a quasi-rectangular wave function between a minimum and a maximum rate of 0 and 1 sccm. The two monolithic films TiAl and TiAlN were prepared using a constant nitrogen flow rate of 0 and 1 sccm, respectively. The maximum N₂ flow rate was high enough to sputter the target in the nitride mode to obtain nitrogen stoichiometry coatings. In the case of multilayers coatings, based on the deposition rate of the $\text{Ti}_{0.67}\text{Al}_{0.33}$ and $\text{Ti}_{0.54}\text{Al}_{0.46}\text{N}$ monolithic films, the pulse periods of 44 s, 90 s, 160 s and 480 s were chosen to obtain stacking periods $\Lambda = 4, 10, 16$ and 50 nm respectively. Two monolithics and multilayers with four different expected period Λ , summarised in Table 1, were as deposited.

Sample name	Stacking	Period Λ (nm)	Thickness ep (nm)
TiAl	TiAl	/	2500
TiAlN	TiAlN	/	2950
ML4	[TiAl/TiAlN]	4	1850
ML10	[TiAl/TiAlN]	10	1790
ML16	[TiAl/TiAlN]	16	1970
ML50	[TiAl/TiAlN]	50	2000

Table 1: Characteristics of monolithic (TiAl and TiAlN) and multilayer (ML4 to ML50) samples deposited by RGPP.

2.2 X-ray diffraction

The samples described above were microstructural analysed by XRD in order to determine their crystallographic lattice and preferential growth directions. The XRD patterns were recorded at room temperature using a Rigaku Smartlab X-ray diffractometer equipped with a CuK α 1 source ($\lambda = 1.54056 \text{ \AA}$) and a Ge (220) two-bounce front monochromator in θ - 2θ parallel mode.

2.3 TEM and EELS

The multilayers have been studied at the atomic scale by TEM, using a doubled corrected ARM 200CF JEOL microscope in Scanning mode (STEM) with a probe size of 0.15 nm operating at 200 kV, on cross-sections. These cross-sections have been prepared by mechanical polishing or Focus Ion Beam (FIB) milling. The chemistry of the nanolayers were probed by EELS. The EELS profiles were acquired along the growth direction in the energy range between the N K-edge and Ti K-edge electron energy loss, with the Quantum Gatan Imaging Filter spectrometer.

2.4 Nanoindentation

The samples have been mechanically characterised by nanoindentation. An Anton Paar ultra-nanoindenter was used. The indentations were realised with a Berkovich tip, whose shape was calibrated by indenting fused silica. Constant strain rate loading ($\dot{P} = 0.05$, with P the load applied on the indenter) associated with continuous stiffness measurements was performed. The load-displacement curves obtained for TiAlN and TiAl enabled the evaluation of the hardness and elastic moduli of these two materials using Oliver and Pharr method [26,27]: a Poisson's ratio of 0.25 for TiAl and 0.21 for TiAlN were assumed [28–30]. The Young's modulus E is deduced from reduced modulus E_r assuming that ν is known, which is the only quantity measured by indentation since E and ν can't be deconvoluted. It can be expressed by:

$$E_r = \frac{E}{(1 - \nu^2)} \quad (1)$$

In order to complete the characterisation made by indentation, a finite element model of the indentation test has been used. This model has been already presented elsewhere by Giljean et al. [13]. It allows to determine the plastic behaviour of a monolithic of TiAlN and TiAl coatings at the mesoscopic scale using the Finite Element Model Updating (FEMU) method. In these works, the

elastic-plastic behaviour of each material is driven by four parameters: the Young's modulus E , the Poisson's ratio ν , the initial yield stress σ_y and a linear hardening modulus H_p (Table 2).

Parameters	TiAl	TiAlN
Yield stress σ_y (GPa) [13]	3.44	14.1
Hardening modulus H_p (GPa) [13]	6.33	34.7
Berkovich Hardness (GPa) [13]	10	31
Elastic Modulus E (GPa) [13]	199	417
Poisson's ratio ν (-) [28–30]	0.25	0.21
Reduced modulus E_r (GPa) [13] (equation (1))	212	436

Table 2 : Elastic-plastic properties derived from literature [9, 23–25]

2.5 Optimization of Knoop hardness by DFT and determination of TiAl and TiAlN properties from microscopic to macroscopic scale

In order to obtain the coating with the best mechanical properties, it has been decided to optimize the Knoop hardness of the TiAl and TiAlN structures. This optimisation based on the crystallographic structures of TiAl and TiAlN was carried out using USPEX software [21,22,31] coupled to VASP (Vienna Ab-initio Simulation Package) software [32,33] using density functional theory. Knoop hardness is determined by the following equation:

$$H_K = \frac{423.8}{V} n \left(\prod_{k=1}^n N_k \sqrt{\frac{X_i^k X_j^k}{CN_i^k CN_j^k}} e^{-2.7 \frac{X_i^k - X_j^k}{4 \sqrt{X_i^k X_j^k}}} \right)^{1/n} - 3.4 \quad (2)$$

with X_i^k and X_j^k the electronegativity of the atoms i and j and for bonds of type k , CN_i^k and CN_j^k the coordination of the atoms, n the bonds quantity and V the lattice volume [19,23]. At the end of the various calculation stages, a TiAl and a TiAlN structure were obtained.

The structures obtained by USPEX are periodic and free of stacking defaults, grain boundaries, etc. So, such structures correspond to an ideal material and cannot be representative of real systems. In order to study the properties of the material, it is therefore necessary to convert the results from a single crystal at the microscopic scale to a macroscopic crystal aggregate. The transition from the micro to the macroscopic domain is achieved using the Voigt-Reuss-Hill methods [17,20]. This method provides an approximation of the mechanical properties of a structure using the coefficients of its elastic tensor C_{ijkl} , which characterise the elastic behaviour of the structure according to the following equation:

$$\sigma_{ij} = C_{ijkl} \epsilon_{kl} \quad (3)$$

where σ_{ij} are the stress tensor components and ϵ_{kl} the strain tensor components.

Voigt method [17] consists on calculating the average of the constraint relationships in a single crystal across all possible orientations of the Bravais lattice on the assumption that the strain is uniform in the whole aggregate. The Reuss method [20] averages the stress relationships based on the stress given in a single crystal, which assumes that the stress is uniform throughout the aggregate. Both methods are approximative, but give a framework of the experimental moduli [18], Voigt values being higher :

$$K_R \leq K \leq K_V \text{ and } G_R \leq G \leq G_V \quad (4)$$

Where K is the bulk modulus and G is the shear modulus. The suffixes V and R denote values calculated according to Voigt's and Reuss's theories. Hill approximation consists of the average value of the Voigt and Reuss values. The different Voigt and Reuss coefficients can be calculated using the following equations [20]:

$$\begin{aligned} 15G_V &= (C_{11} + C_{22} + C_{33}) - (C_{12} + C_{23} + C_{31}) + 3(C_{44} + C_{55} + C_{66}) \\ 15/G_R &= 4(S_{11} + S_{22} + S_{33}) - 4(S_{12} + S_{23} + S_{31}) + 3(S_{44} + S_{55} + S_{66}) \\ 9K_V &= (C_{11} + C_{22} + C_{33}) + 2(C_{12} + C_{23} + C_{31}) \\ 1/K_R &= (S_{11} + S_{22} + S_{33}) + 2(S_{12} + S_{23} + S_{31}) \end{aligned} \quad (5)$$

Where $C_{\alpha\beta}$ are the stiffness constants and $S_{\alpha\beta}$ the flexibility constants in the Voigt notation such that $\epsilon_\alpha = S_{\alpha\beta}\sigma_\beta$.

From K and G , Young's modulus E and Poisson's ratio ν_0 can be determined by the following equations:

$$E = \frac{9KG}{3K + G} \quad (6)$$

$$\nu_0 = \frac{3K - 2G}{6K + 2G} \quad (7)$$

The Vickers hardness is calculated with the semi-empirical model of Mazhnik and Oganov [19,23] using the following equation:

$$H_V = \frac{96E(1 - 8.5\nu_0 + 19.5\nu_0^2)}{9.81(1 - 7.5\nu_0 + 12.2\nu_0^2 + 19.6\nu_0^3)} \quad (8)$$

Fracture toughness K_{IC} can be determined by the following equation [19]:

$$K_{IC} = \alpha_0^{-\frac{1}{2}} V_0^{1/6} [\zeta(\nu_0)E]^{3/2} \quad (9)$$

Where $\alpha_0 = 8840$ GPa is a parameter depending on the chemical bonding in the material and has a unit of pressure, V_0 is the volume per atom and $\zeta(\nu_0)$ is a dimensionless function of Poisson's ratio ν_0 . It can be expressed as follows:

$$\zeta(\nu_0) = \frac{1 - 13.7\nu_0 + 48.6\nu_0^2}{1 - 15.2\nu_0 + 70.2\nu_0^2 - 81.5\nu_0^3} \quad (10)$$

All of these calculations can be achieved using HardnessML software [19,23,34,35]. This software only needs the atomic coordinates to calculate the mechanical properties of the structures. An elastic tensor of a structure close to the ones submitted is taken from the materials project database [36] and used for the calculations. This can result in approximation in the mechanical properties of the first place. Moreover, the software gives only the Hill approximation of the

mechanical properties. Thus, the range within which the mechanical properties are found cannot be studied.

2.6 Molecular dynamics

Interfaces between TiAl and TiAlN were constructed in accordance with experimental observations made by X-ray diffraction by stacking several TiAlN and TiAl unit cells. TiAlN nitride and TiAl metal crystallise in a face-centred cubic (fcc) and a hexagonal (hcp) lattice respectively. XRD results showed that in a TiAlN/TiAl multilayer coating, the TiAl layers grow in the direction $[002]_h$, while the TiAlN layers grow in the directions $[200]_c$ and $[111]_c$. It results in many stacking possibilities depending on the surface group of TiAlN and TiAl. In the case of a TiAlN $[111]_c$ growth, 23 stackings have been identified, and 40 in the case of a TiAlN $[200]_c$.

In this work, two stacks were selected to construct a slab based on their total energy and initial hardness. A first stacking $[111]_c/[002]_h$ named I_{111} with a thickness of ~ 6 Å and ~ 9 Å respectively with 2 Å of vacuum between the two materials to facilitate the atom migration by MD. It consists of 912 atoms, including 454 titanium atoms, 266 aluminium atoms and 192 nitrogen atoms. A second stacking $[200]_c/[002]_h$ named I_{200} with a thickness of ~ 8 Å and ~ 11 Å respectively with ~ 2 Å of vacuum between the two materials. It consists of 460 atoms, including 204 titanium atoms, 128 aluminium atoms and 128 nitrogen atoms. The two stacks were then relaxed by molecular dynamics at a target temperature of 300 K to monitor the evolution of the nitrogen concentration at the interface using the DFT SIESTA calculation code.

The aim of molecular dynamic is to characterise the forces that enable particle movement, which involves solving Newton's equation of motion.

$$\vec{F}(t) = -\vec{\nabla}E = m\vec{a}(t) = m \frac{d^2\vec{r}(\vec{t})}{dt^2} \quad (11)$$

Where F is the total force exerted on the system, m is the mass of the particle and $\vec{\nabla}E$ the energy gradient, t the time, $\vec{r}(\vec{t})$ the position and $\vec{a}$ the acceleration.

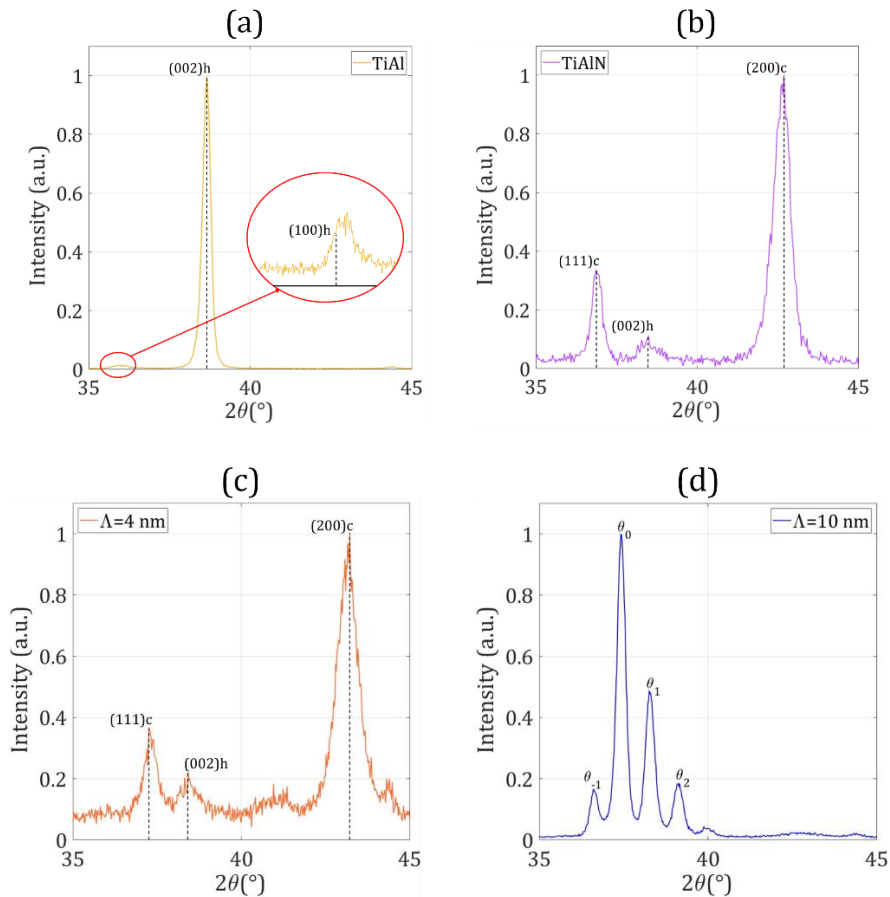
Forces are calculated by deriving an Embedded Atom Model (EAM) interatomic potential [38], an approximation describing the energy between atoms and behaving like an interatomic potential. SIESTA uses pseudopotentials that preserve the norm in their entirely non-local form. It also uses a basis set of finite support atomic orbitals, and the wave functions and electron density are projected onto a grid in real space in order to calculate exchange-correlation and Hartree potentials and their matrix elements. The fineness of the grid, and as such the resolution of the real space, depends on the MeshCutoff parameter. [39–41]

This relaxation was performed using pseudo potentials GGA (Generalised Gradient Approximation) for Ti, Al, N in SZP (Single Zeta Polarised) basis with a MeshCutoff of 100 Rydberg (Ry), and a maximum tolerance on the force of 0.02 eV/Å. [42,43].

3 Results and discussion

3.1 Micro and nanostructural characterisation (XRD, TEM and EELS)

The XRD patterns are shown on Figure 1. The pattern of the monolithic $\text{Ti}_{0.66}\text{Al}_{0.33}$ coating (Figure 1a) shows a main peak attributed to the $[002]_h$ direction and a second peak in the insert attributed to the $[100]_h$ direction of a hexagonal structure. The deduced interplanar distance, calculated using Bragg's formula, are $a = 2.87 \pm 0.01 \text{ \AA}$ and $c = 4.64 \pm 0.01 \text{ \AA}$. The monolithic $\text{Ti}_{0.54}\text{Al}_{0.46}\text{N}$ coating (Figure 1b) exhibits two main peaks attributed to $[111]_c$ and $[200]_c$ growth directions of fcc crystal structure. The corresponding lattice parameters calculated are $a_{111} = 4.21 \pm 0.01 \text{ \AA}$ and $a_{200} = 4.23 \pm 0.01 \text{ \AA}$. A bump at $2\theta \sim 38.5^\circ$ is attributed to the 45-nm-thick TiAl underlayer. The 4 nm-period film (Figure 1c) shows both TiAl hexagonal and TiAlN cubic structures. The 10- and 16-nm-period films (Figure 1d and Figure 1e respectively) show typical patterns of a superlattice with a main peak flanked by satellites. Finally, the 50 nm-period pattern (Figure 1f) clearly displays two distinct peaks ascribed to $[111]_c$ and $[002]_h$ of cubic and hexagonal structures respectively.



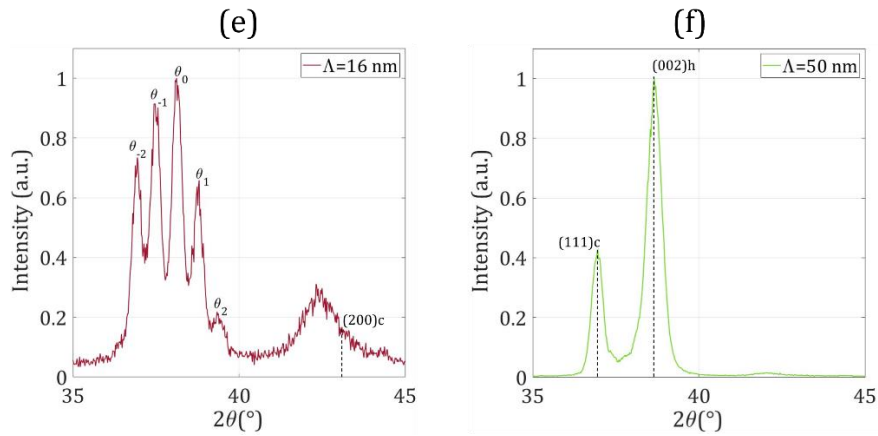


Figure 1: XRD patterns of monolithic (a) TiAl and (b) TiAlN coatings and TiAl/TiAlN multilayer coatings with different Λ periods (c) 4 nm, (d) 10 nm, (e) 16 nm and (f) 50 nm.

Annular Dark Field STEM images of the cross-section of the multilayer are shown on Figure 2. The multilayers clearly exhibit alternating of brighter (with no or lowest nitrogen content) and darker (with highest nitrogen content) nanolayers, characteristic of a multilayer stacking. The composition of the nanolayers was calculated from EELS profiles (Figure 3). For the 50 nm-period (Figure 3c), a regular multilayer coating is visible with alternating nanolayers of the metal and the nitride in the stacking separated by transition zones measuring a few nanometres. The 10 nm-period sample show a multilayer staking with the presence of nitrogen (about 35%) even within the expected metal nanolayers (Figure 3b). This observation is more remarkable in the 4 nm-period which exhibits imbalanced thicknesses of the nanolayers and a relative concentration of nitrogen of more than approximately 60% (Figure 3a).

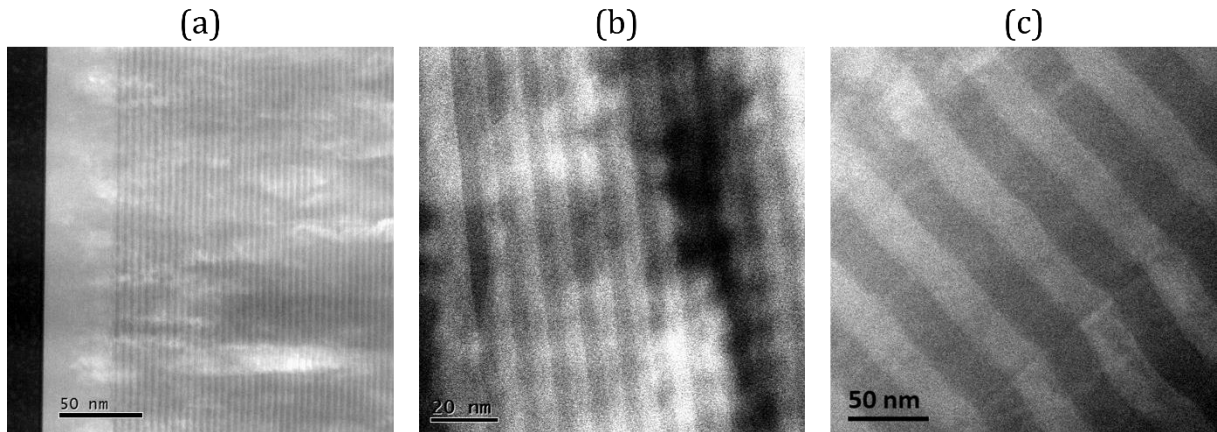


Figure 2: Annular Dark-field STEM image of the cross-section of TiAl/TiAlN multilayered film (a) FIB lamella $\Lambda = 4$ nm (b) mechanically polished lamella $\Lambda = 10$ nm, (c) FIB lamella $\Lambda = 50$ nm.

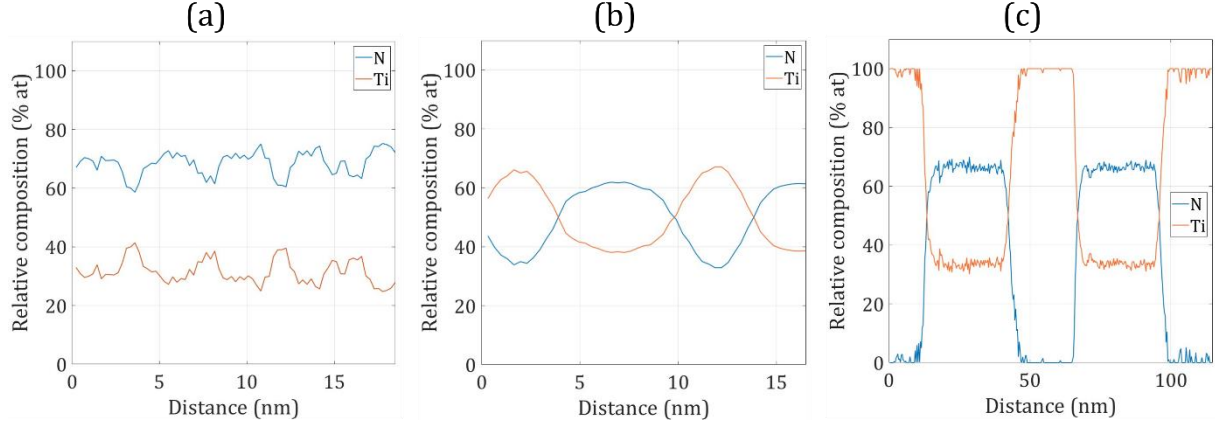


Figure 3: Relative concentration of N and Ti elements extracted from EELS profiles of the (a) $\Lambda = 4$ nm, (b) $\Lambda = 10$ nm, (c) $\Lambda = 50$ nm multilayer coatings

3.2 Analytical analysis of the depth sensing measurement

From indentation experiments, both elastic modulus and hardness can be extracted as a function of the penetration depth (Figure 4). As previously mentioned in the introduction, hardness and indentation modulus depend on the periods of the coatings, indicating a clear effect of hardening/stiffening as the period decreases [3–7,11,13]. Hardness and indentation modulus were extracted using a thin film model largely inspired of King [44–46]. Here, the composite mechanical property P_c (hardness or indentation modulus) measured by indentation is expressed as a function of the properties of the film P_f and the substrate P_s (equations (12) and (13)):

$$\frac{1}{P_c} = \frac{\Phi_P}{P_s} + \frac{1 - \Phi_P}{P_f} \quad (12)$$

$$\Phi_P = \exp \left(-a_P \left(\frac{ep}{h} \right)^{n_P} \right) \quad (13)$$

Where the function Φ_P characterizes the evolution of the studied system property transitioning from the film's behaviour at $h = 0$ to that of the substrate as $h = \infty$. Indeed Φ_P tends to 0 when h tends to zero, and Φ_P tends to 1 for high indentation depth. It depends on the film thickness ep and the indentation depth h . The parameters a_P and n_P are two constants depending on the coatings and the mechanical property under consideration. The properties (once again hardness or indentation elastic modulus) of the TiAlN/TiAl multilayer film ($\bar{p}$) depends on the one of the single layers TiAl (p_{TiAl}) and TiAlN (p_{TiAlN}) following rule of mixture driven by the volume fraction of TiAlN V_f (equation (14)):

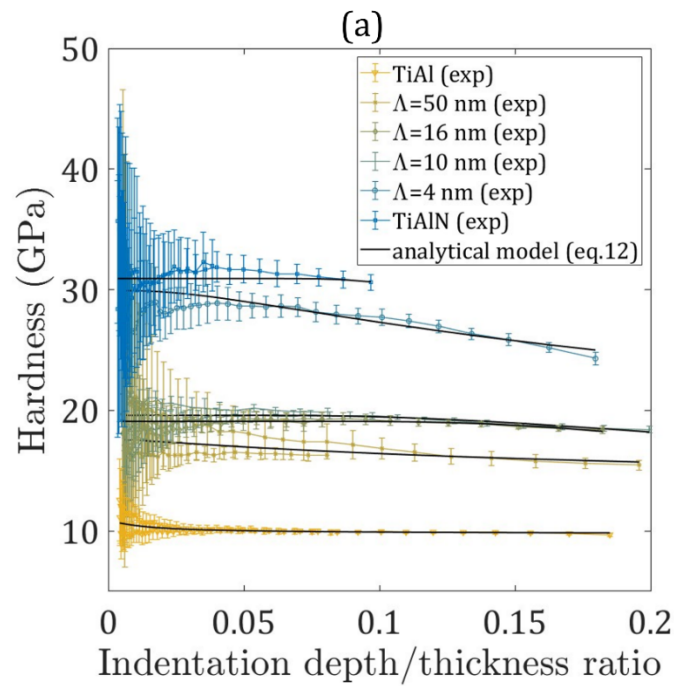
$$\frac{1}{\bar{p}} = \frac{V_f}{p_{TiAlN}} + \frac{1 - V_f}{p_{TiAl}} \quad (14)$$

$$V_f = \frac{e_{TiAlN}}{e_{TiAlN} + e_{TiAl}} \quad (15)$$

From the value of V_f , it is also possible to calculate e_T , the additional thickness of TiAlN that this would represent around each interface, using the following equation:

$$e_T = (V_f - 0.5) \frac{\Lambda}{2} \quad (16)$$

This model is fitted to the experimental indentation modulus and hardness data obtained from the four multilayer coatings and the two monolithic TiAl and TiAlN. Figure 4 shows that the model fits the experimental data well, both for Hardness and Indentation modulus. The main fitting parameters derived from this analysis are summarised in Table 3 and Table 4.



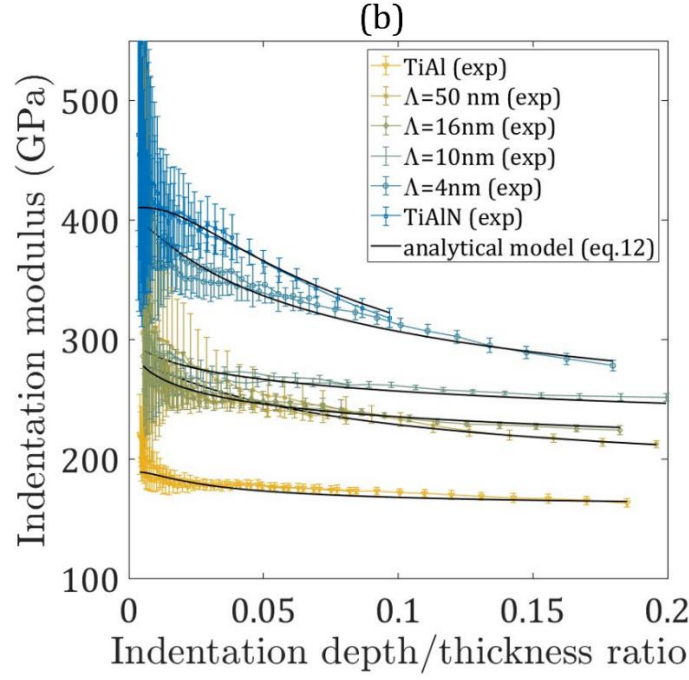


Figure 4: Experimental and modeled (a) hardness and (b) indentation modulus depending on indentation depth over film thickness ratio (h/ep) for monolithic TiAlN, TiAl and TiAlN/TiAl multilayers.

Properties	E_{TiAl}	E_{TiAlN}	H_{TiAl}	H_{TiAlN}
Values (GPa)	195	431	11	31

Table 3: Mechanical properties of the adjusted analytical model. E correspond to Young's modulus, H to Berkovich hardness.

Period Λ	4 nm	10 nm	16 nm	50 nm
Vf_a	98%	69%	67%	59%
e_{Ta}	0.96 nm	0.95 nm	1.36 nm	2.25 nm

Table 4: Analytically identified volume fraction of nitride Vf_a ($Vf = Vf_a$ in equation (15)) in the Λ period multilayer coating ($\Lambda = 4, 10, 16, 50$ nm) and the associated additional thickness of TiAlN e_{Ta}

The different values of the TiAlN volume fraction (V_f , noted here Vf_a) shown in Table 4 are all superior to 50%. It suggests a strong imbalance between TiAl and TiAlN in the coating. To directly quantify this imbalance from the mechanical response of the different coatings rather than relying on hardness or indentation modulus measurements, a numerical finite element model of the multilayer system was developed to simulate the indentation force–displacement response of the various films [13].

3.3 Volume fraction of TiAlN obtained with the homogenised multilayer coating

Implementing the geometry of the coating layer by layer from the substrate can lead, in the case of a small period, to a very heavy numerical model in terms of finites elements number. To overcome this difficulty, a single homogenised coating is proposed (Figure 5). As described by equation (14), the mechanical properties of this equivalent coating are determined using a rule of mixtures, assuming that TiAl and TiAlN act in series. The homogenised model is adjusted by calibrating the indentation curves, what is achieved by varying the volume fraction V_f of TiAlN within the coating (Figure 5). This rule of mixtures is applied to all the parameters of the plastic bilinear law introduced previously in Section 2.4 (Table 2).

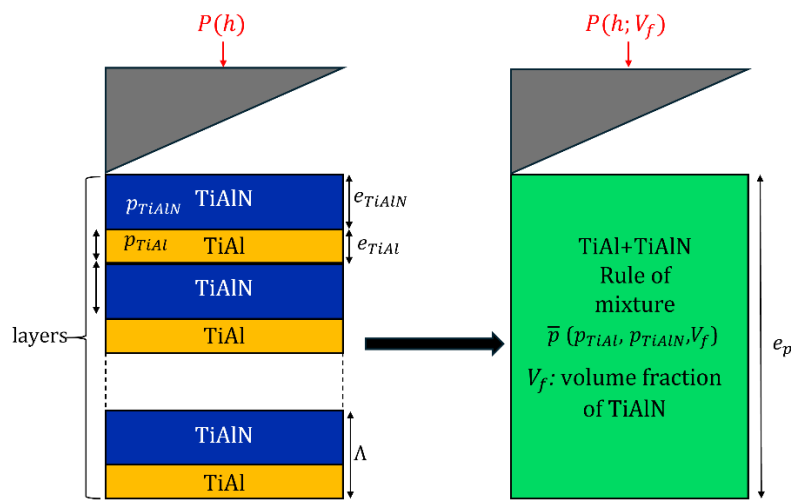


Figure 5: Schematic representation of the homogenised coatings under indentation. e_{TiAlN} and e_{TiAl} correspond to TiAlN and TiAl layer thickness respectively, p_{TiAlN} and p_{TiAl} correspond to TiAlN and TiAl mechanical properties respectively and $\bar{p}$ to the elastoplastic properties (E, ν, σ_y, H_p) of the homogenised material.

The values of V_f have been identified for each multilayer coating by the FEMU method. They have been named $V_{f_{FEM}}$. This implies minimizing the gap between numerical and experimental indentation response [47]. The results are plotted on Figure 6. All identified $V_{f_{FEM}}$ values have been listed in Table 5.

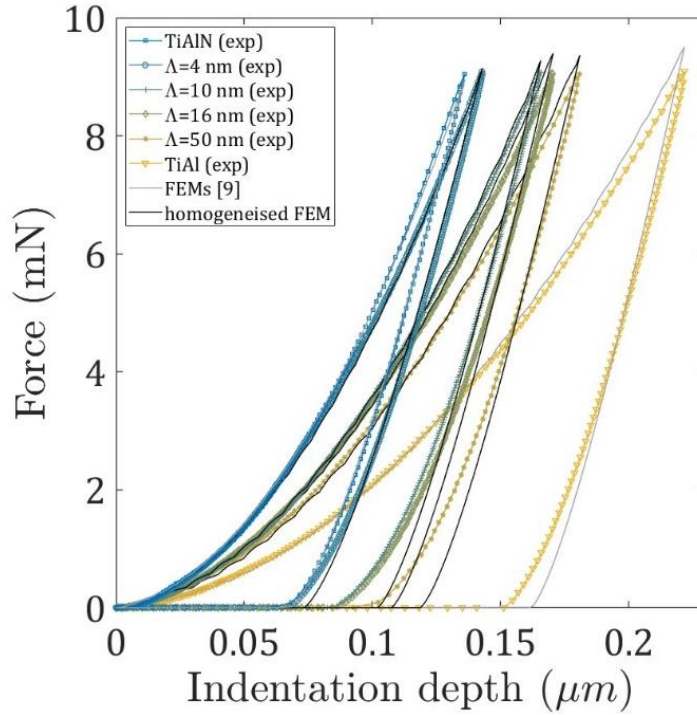


Figure 6: Indentation curves of the different period samples simulated using the homogenised model compared with the experimental indentation curves

The Vf_{FEM} values are higher than 50%, whatever the period of the multilayer, which suggest an imbalance of TiAl and TiAlN nanolayer thicknesses within the stacks. As the Λ period decreases, Vf_{FEM} increases, reflecting an increase in the proportion of TiAlN in the coating. It explains the ultra-hard nature of coatings with very short periods. It is interesting to note that the values of Vf_{FEM} determined via FEMU are similar to the Vf_a determined with the analytic thin film model described in part 3.1. As the formation of nitride in the deposition chamber comes from the nitrogen pulsed during the RGPP process, for short periods, the time taken to shut off the nitrogen flow is not sufficient for complete decontamination of the chamber despite pumping. Then, it can be observed that the imbalance between TiAlN and TiAl increases when the period decreases, as expected because of the multiplication of the interfaces. Finally, it is also interesting to observe that, when this imbalance is converted into a thickness, the value of this additional thickness is not constant suggesting that different mechanisms act at the nanometric scale depending on the period of the multilayer.

Period Λ	4 nm	10 nm	16 nm	50 nm
Vf_{FEM}	97%	73%	69%	57%
e_{TFEM}	0.94 nm	1.15 nm	1.52 nm	1.75 nm
Difference with analytical model	2%	21%	12 %	22 %

Table 5: Vf_{FEM} values obtained for different samples, e_{TFEM} , the associated additional thickness of TiAlN, and the difference with the analytical model from section 3.2

3.4 TiAl and TiAlN properties obtained by DFT

Figure 7 shows the structure of TiAl and TiAlN computed by DFT. Their structural characteristics are summarised in Table 6 together with the ones determined by XRD. The structures obtained by DFT have structural characteristics similar to those analysed by XRD. The lattice parameters obtained via DFT are close to the ones found by XRD, with a difference of 2% for c , and 7% for a (hexagonal lattice parameter of TiAl) and no difference for a TiAlN (fcc lattice parameter). The ratio of the hexagonal lattice parameters c/a of TiAl obtained with DFT is close to the one obtained with XRD data, being respectively 1.69 and 1.61. Both values are close to 1.63, which is the theoretical value of a hexagonal structure.

However, differences between the mechanical properties of the structure obtained by DFT and the experimental results exist. The properties calculated by DFT are listed in Table 7. A difference of 27% exists between Young's moduli. Two factors can mainly explain this gap. The first one is that the Young's modulus obtained numerically is calculated using the Hill approximation which assumes a polycrystal without defects with random crystallographic orientations while the indentation modulus is far to be a standard parameter when the studied materials present a great anisotropy [48]. The second factor is inherent to the instrumented indentation method. In fact, indentation elastic modulus, as well as hardness, is known to be strongly dependent on the contact area evaluation, and therefore on the presence or absence of pile-up between the indenter and the material. The presence of pile-up when the maximum force is applied is complicated to verify experimentally. However, if the intrinsic values of the modulus are different, the different ratios between the elastic moduli of TiAl and TiAlN presented in Table 8 are the same experimentally and numerically, thus reinforcing the comparisons made previously on the TiAl and TiAlN structures.

In the case of hardness, the difference is even more pronounced. For example, the hardness obtained numerically is half of the one obtained experimentally. The ratio of the hardness between TiAl and TiAlN is also different. The numerical value is 0.47, compared to 0.32 experimentally. This discrepancy can be attributed mainly to the theoretical models used to calculate plastic properties using semi-empirical methods [49].

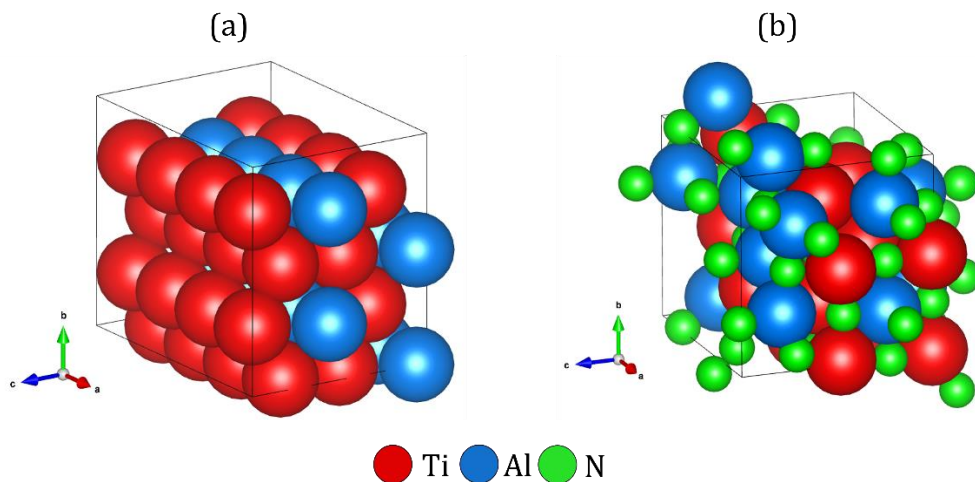


Figure 7: Representation with VESTA [50] of the (a) TiAl and (b) TiAlN structures computed by DFT

	TiAl (DFT)	TiAl (XRD)	TiAlN (DFT)	TiAlN (XRD)
Structure	Hexagonal		Face centred cubic	
Space group	191	/	1	/
Lattice parameters	$a = 2.68 \text{ \AA}$	$a = 2.87 \text{ \AA}$	$a = 4.23 \text{ \AA}$	$a = 4.23 \text{ \AA}$
	$b = 4.53 \text{ \AA}$	$b = /$	$b = 4.33 \text{ \AA}$	/
	$c = 4.54 \text{ \AA}$	$c = 4.64 \text{ \AA}$	$c = 4.26 \text{ \AA}$	/
	$\alpha = 90^\circ$	/	$\alpha = 88.7^\circ$	/
	$\beta = 90^\circ$	/	$\beta = 90^\circ$	/
	$\gamma = 90^\circ$	/	$\gamma = 89.6^\circ$	/
Volume	$765 \text{ \AA}^3$	/	$624.77 \text{ \AA}^3$	/
Density	4.262 g/cm^3	/	4.430 g/cm^3	/

Table 6: Structural characteristics of TiAl and TiAlN structures computed by DFT and measured by XRD

	TiAl	TiAlN
Bulk modulus (GPa)	108.8	235.1
Shear modulus (GPa)	62.1	128.8
Young modulus (GPa)	156.5	326.8
Poisson's ratio (-)	0.26	0.27
Vickers Hardness (GPa)	7.4	15.8
Fracture toughness ($\text{MPa}\sqrt{\text{m}}$)	0.9	2.7
Reduced modulus (GPa)	167.8	352.5

Table 7: Mechanical properties of TiAl and TiAlN structures computed by DFT

	Ratio ⁺	ratio exp [#]
Bulk modulus (GPa)	0.46	/
Shear modulus (GPa)	0.48	/
Young modulus (GPa)	0.48	0.48
Poisson's ratio (-)	0.97	/
Vickers Hardness (GPa)	0.47	0.32
Fracture toughness ($\text{MPa}\sqrt{\text{m}}$)	0.33	/
Reduced modulus (GPa)	0.48	0.49

Table 8: Ratios between the mechanical properties of TiAl and TiAlN structures obtained by DFT⁺ and nanoindentation[#]

3.5 Mechanical and structural characteristics of the interfaces rearranged by molecular dynamics

The interfaces were constructed using the PyMatgen software and were analysed through DFT relaxation to determine their structural characteristics. MD calculations allow to obtain a thermodynamically stable structure by minimisation of the internal energy of both interface types. Figure 8 illustrates the evolution of the internal energy per atom as the simulation progresses. Upon completion of the calculations, it was observed that the I_{111} interface exhibits a higher absolute internal energy than the I_{200} interface, indicating that the latter is thermodynamically more stable. These results confirm that the growth direction of the TiAlN layer significantly influences structural stability.

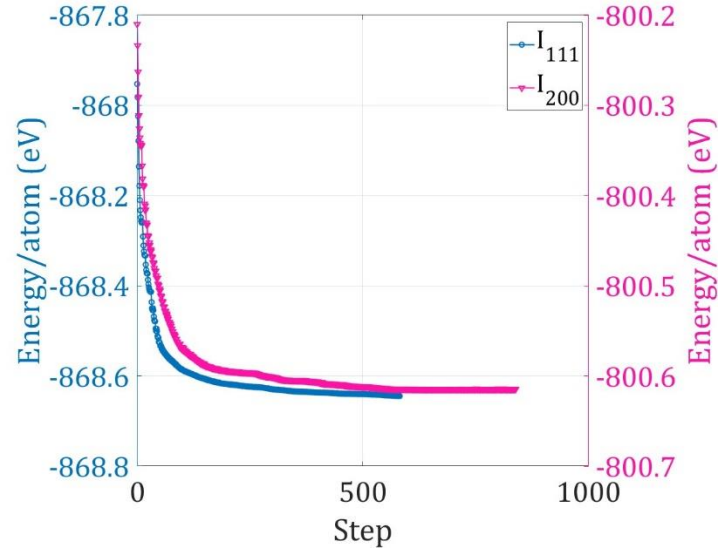


Figure 8: Energy evolution per atom as a function of the relaxation time step of both interfaces I_{111} and I_{200} .

During the relaxation, the morphology of each layer is changed due to atoms migration. It also enables to define and isolate a new transition layer whose thickness is controlled by the nitrogen atoms that have diffused deepest into the TiAl layer. To analyse the evolution of the displacements of atoms during relaxation, the TiAlN layer has been isolated. Figure 9 shows the structures before and after relaxation alongside the isolated TiAlN layers.

The new TiAlN layer induced by relaxation is composed, in the case of I_{111} , of 108 titanium atoms, 126 aluminium atoms and 192 nitrogen atoms, and in the case of I_{200} , of 69 titanium atoms, 59 aluminium atoms and 128 nitrogen atoms.

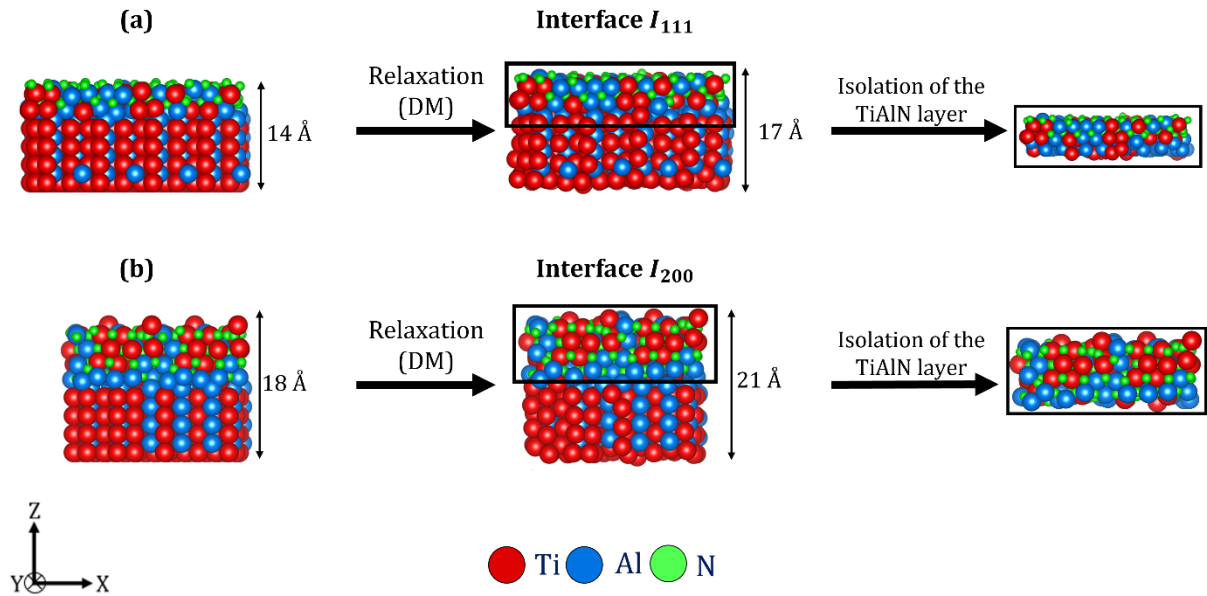
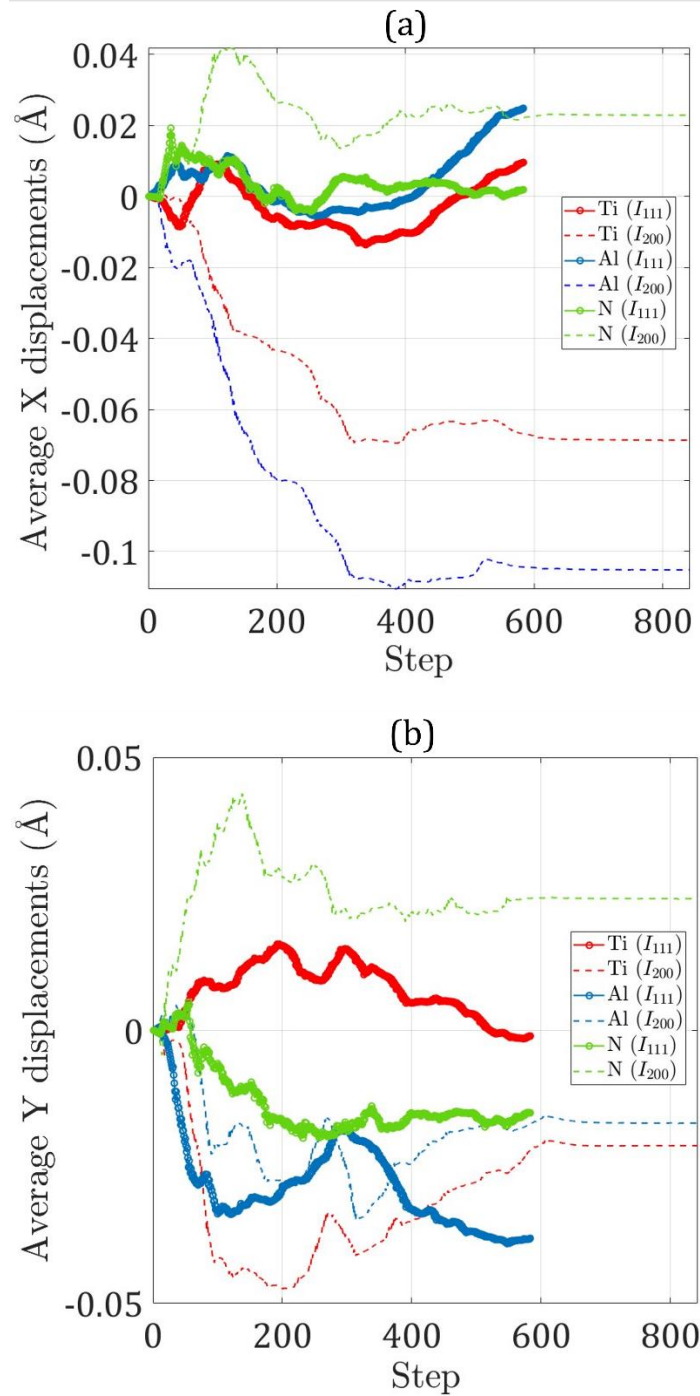


Figure 9: Interfaces (a) I_{111} and (b) I_{200} before and after relaxation by molecular dynamic (DM)

The positions of all atoms have been compared with the initial set position. Figure 10 shows the amplitude of the average atom's displacements of both interface I_{111} and I_{200} . For both interfaces (i.e I_{111} and I_{200}), atom migration occurs mostly during the first 100 relaxation steps. The greatest displacements occur in the Z direction for nitrogen and aluminium, and in the X and Z direction for titanium. For the I_{111} , the nitrogen atom's average displacement is the greatest of them all, reaching $-0.31 \text{ \AA}$, while for I_{200} the greatest displacement is observed for aluminium atoms, reaching $-0.29 \text{ \AA}$. However, Figure 10c also clearly shows that the Z displacement of the N atoms is opposite to the ones of the Ti and Al atoms for both interfaces. A differential displacement of almost $0.5 \text{ \AA}$ is observed between N and Ti/Al atoms for both cases.



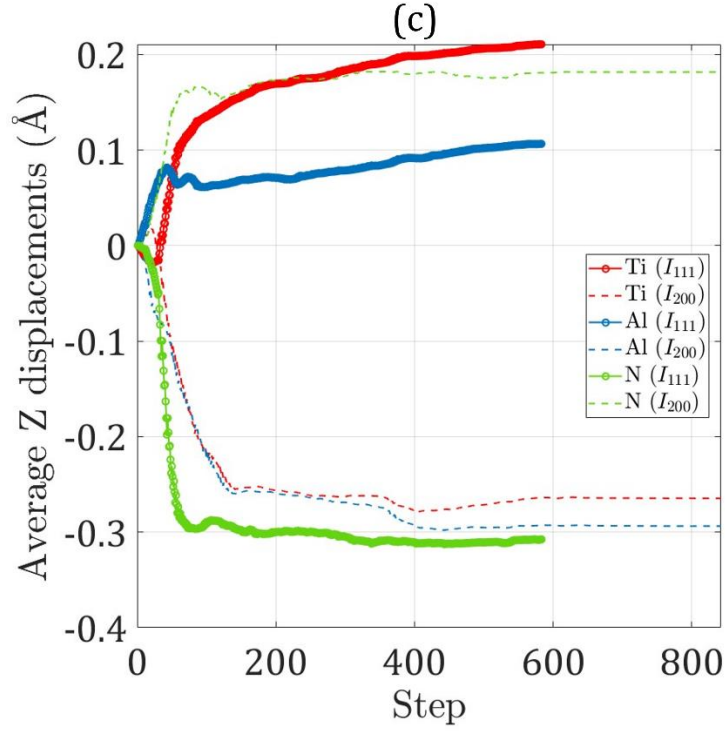


Figure 10: Average displacement (in Angstrom) of all atoms of each type from the interface I_{111} and I_{200} over time for (a) X (b) Y and (c) Z

To evaluate the evolution of the nitrogen (N) atomic concentration as a function of depth (z), the slab was partitioned into 1 Å increments across three stacked layers for the I_{111} and I_{200} interfaces (Figure 11a and Figure 11b, respectively). The resulting profiles reveal distinct behaviours dictated by interface orientation and transition direction. Specifically, the I_{111} orientation displays a marked asymmetry, where the nitrogen concentration gradient is steeper in the $\text{TiAlN} \rightarrow \text{TiAl}$ transition than the $\text{TiAl} \rightarrow \text{TiAlN}$ transition. A similar trend is observed for the I_{200} interface. Ultimately, these results indicate that regardless of crystallographic orientation, the nitrogen concentration gradient is systematically lower when transitioning from metal to nitride than when transitioning from nitride to metal, suggesting that the former interface is consistently less abrupt.

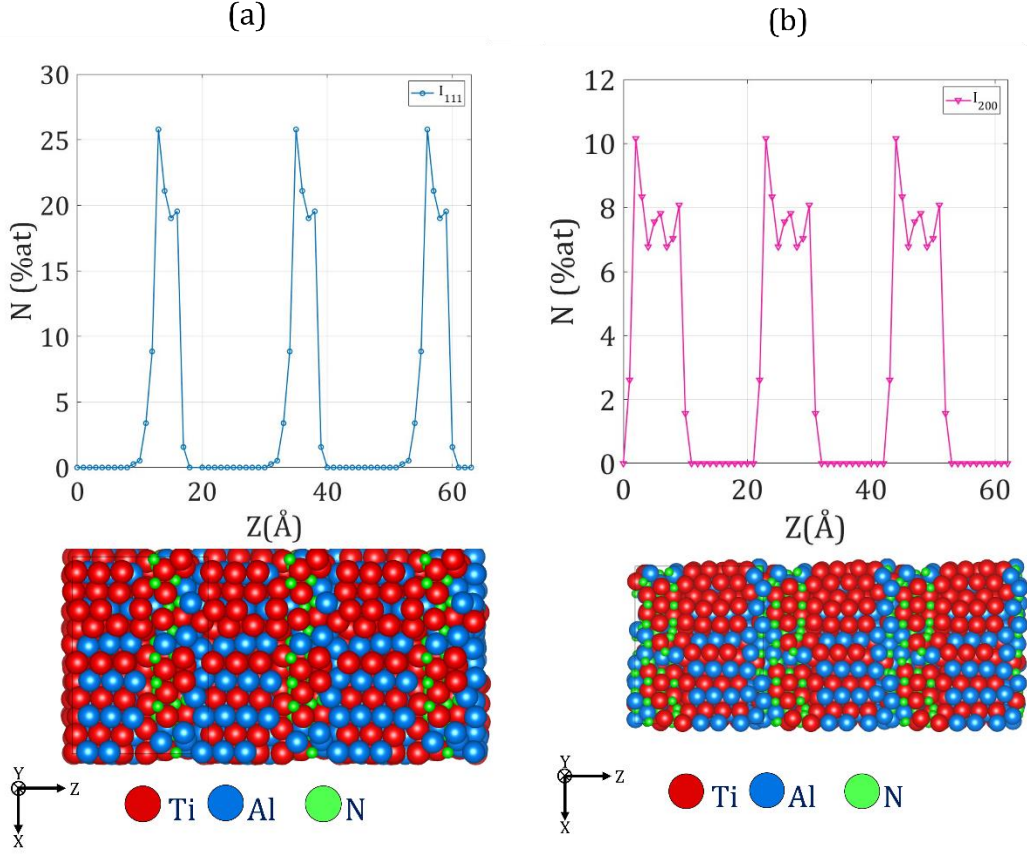


Figure 11: Atomic nitrogen concentration per angstrom after relaxation in three slabs and the representation of (a) the I_{111} interface and (b) the I_{200} interface

The mechanical properties of both I_{111} and I_{200} interfaces have been calculated using HardnessML software. Based on the mechanical properties of TiAlN p_{TiAlN} and TiAl p_{TiAl} , the properties $\bar{p}$ of an hypothetical material comprising equal proportions of TiAlN and TiAl were calculated by considering a serie connection via equation (14) with $V_f = 0.5$ and a parallel assembly via equation (17):

$$\bar{p} = V_f p_{TiAlN} + (1 - V_f) p_{TiAl} \quad (17)$$

The properties of this hypothetical material are listed in Table 9 alongside the calculated properties of I_{111} and I_{200} interfaces.

It appears that the interface I_{200} , which grows according to direction $[200]_c$, possesses better mechanical properties than the I_{111} interface, which grows according to direction $[111]_c$. Moreover, both interfaces mechanical properties are superior to the properties of the hypothetical material comprising equal proportions of TiAlN and TiAl in a serie and parallel arrangement. It shows an enhancement of the theoretical mechanical properties of the structure.

	Serie ($V_f = 0.5$)	Parallel ($V_f = 0.5$)	Interface I_{111}	Interface I_{200}
Bulk modulus (GPa)	148.8	172.0	190.7	213.5
Shear modulus (GPa)	83.8	95.5	102.5	115.8
Young modulus (GPa)	211.7	241.7	260.7	294.2
Poisson's ratio (-)	0.26	0.26	0.27	0.27
Vickers Hardness (GPa)	10.1	11.6	12.7	14.3
Fracture toughness ($\text{MPa}\sqrt{\text{m}}$)	1.35	1.80	2.00	2.40

Table 9: Comparison of the mechanical properties of isolated interface layers (I_{111} and I_{200}) and a hypothetical material comprising equal proportions of TiAlN and TiAl in a serie or parallel arrangement.

The V_f values of I_{111} and I_{200} allowing to find the mechanical properties of the interface obtained by DFT with mixture rule have been calculated. These values range from 0.90 to 0.93 for I_{200} and from 0.76 to 0.83 for I_{111} in serie.

As the mechanical properties of the different multilayer increase with decreasing periods, they have been plotted as a function of the inverse of the period. Figure 12a shows the evolution of the hardness and the yield stress of the four multilayers calculated respectively with V_{fa} and V_{fFEM} as a function of $1/\Lambda$. They have been also plotted as a function of $1/\sqrt{\Lambda}$ as it is generally done for multilayer [3] arguing that the hardening mechanism is close to a Hall-Petch effect (Figure 12b). It is interesting to note that the correlation is much better with $1/\Lambda$ than with $1/\sqrt{\Lambda}$ both for hardness and yield stress in accordance with the works of [53–56].

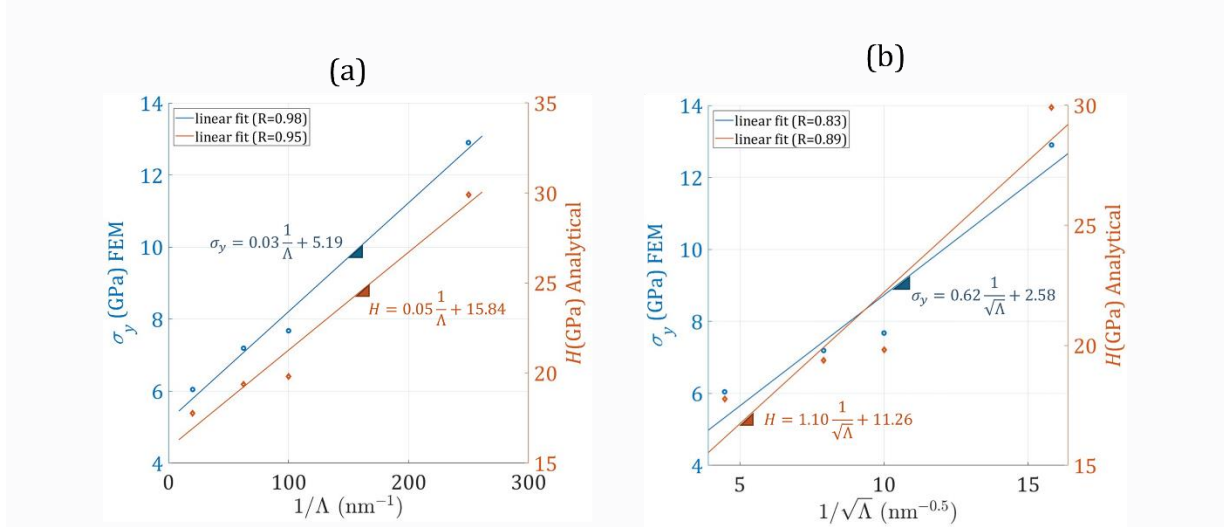


Figure 12: Evolution of σ_y and H as a function of (a) $1/\Lambda$ and (b) $1/\sqrt{\Lambda}$

Interestingly, the same work is performed with V_f . Figure 13 shows the different values of V_f , determined either by the thin film model or by FEMU, plotted against $1/\Lambda$. The range of V_f values determined by MD are also shown on the Figure. Such kind of representation allows to evaluate empirically, only from the value of the period of any multilayer, the coefficient V_f necessary to determine the complete set of parameters (Young modulus, Hardness, Yield stress, hardening modulus).

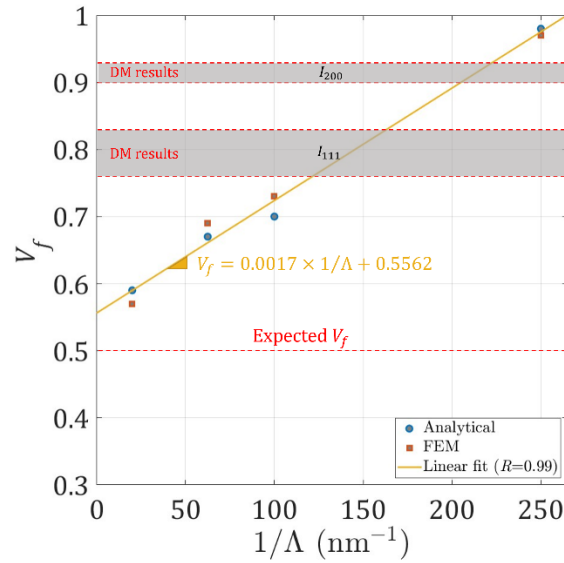


Figure 13: Evolution of V_f depending on $1/\Lambda$ for analytical and FEM results and comparison with a linear regression and the DM results.

Additionally, a similar approach can be envisaged regarding the relation between hardness and yield stress (Figure 14). Including the two monolithic layers studied in this work, a linear relation can be found between hardness and yield stress as it has been firstly proposed by Tabor and widely adopted since [52]. The relation established here allow to determine the yield stress of any TiAl/TiAlN multilayer only from its hardness measurement. It is interesting to note that the encountered slope, 1.9, is different from the one of Tabor, 3.3, or Mata ,2.7 for example. This is not so surprising as the material studied here are very different from the ones addressed in [51,52].

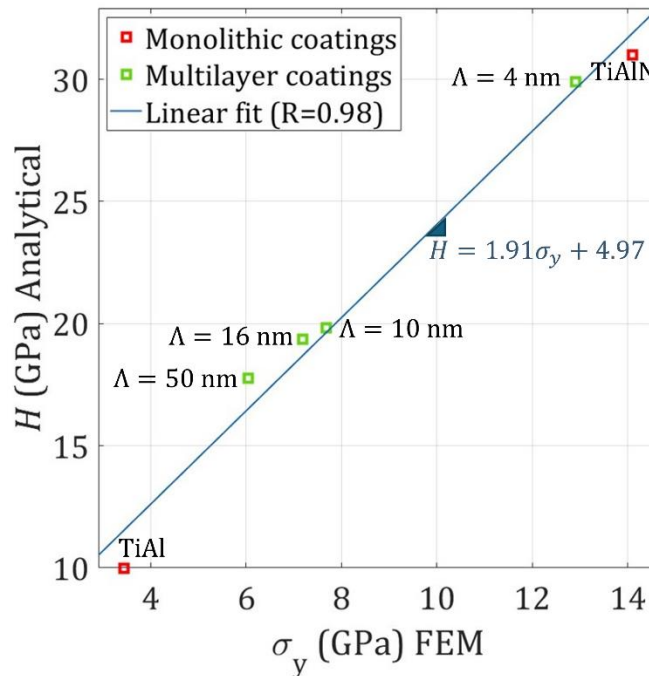


Figure 14: Evolution of Hardness H depending on σ_y

Conclusion

In this paper, the mechanical response of TiAlN/TiAl multilayer deposited by radio-frequency magnetron sputtering has been investigated through a multiscale strategy thanks to experimental, analytical and numerical methods. The following conclusion can be drawn:

- first a top-down approach, based on homogenisation method of a multilayer coating had allowed to evaluate macroscopically the imbalance between TiAl and TiAlN in the multilayer. This has been done following two ways, adjusting the response of the evolution of the hardness and indentation elastic modulus as a function of depth with an analytical model and calibrating a finite element model with the FEMU method on the indentation curves of multilayer having different period. These two methods give very similar results, moreover on different experimental observables, thus reinforcing their validity.

- then, a bottom-up approach by DFT and Molecular Dynamics had allowed to confirm a migration of the nitrogen atoms from the TiAlN layers to the TiAl metal layers. It has been shown that this migration may enhance the mechanical properties of the whole multilayer coating. However, the results obtained by MD show also that this migration of the nitrogen atoms that did not exceed 0.5 Angstrom, suggesting that the main reinforcement mechanism is the nitrogen contamination occurring during the deposition.

So, supported by STEM observations, which confirm the multilayered nature of the coatings, and by EELS concentration profiles which show that nitrogen is present in each of the layers for the shortest periods, we can conclude that for the shortest periods we are no longer dealing with a metal/ceramic multilayer in the strict sense, but rather with a quasi-homogeneous material with a TiAlN_x/TiAlN ($x < 1$) architecture. Finally, all the tools are provided here to predict the mechanical properties (elastic modulus, initial yield stress, hardening modulus) of any TiAlN/TiAl multilayer only from the value of its periods or its hardness.

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Author contributions: CRediT

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