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Microstructure and mechanical property of TiN/AlN multilayered coatings: The impact of AlN thickness

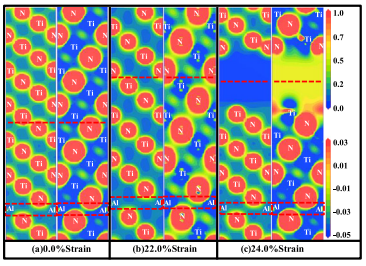
Deqiang Yin [a,*], Yi Yang [a], Xianghe Peng [b], Yi Qin [c], Zhongchang Wang [b,d,**]

[a] School of Manufacturing Science and Engineering, Sichuan University, Chengdu, China
[b] Department of Engineering Mechanics, College of Aerospace Engineering, Chongqing University, Chongqing 400044, China
[c] Department of Design, Manufacture, and Engineering Management, University of Strathclyde, Glasgow G1 1XQ, Scotland, UK
[d] Advanced Institute for Materials Research, Tohoku University, 2-1-1 Katahira, Aoba-ku, Sendai 9808577, Japan

HIGHLIGHTS

- Tensile strength of TiN/AlN system weakens as the AlN thickness increase.
- Fracture mode differs by changing the AlN coating layer.
- Electronic structure variation accounts for the different fracture modes.
- Charge transfer is critical to mechanical behavior during tensile process.

GRAPHICAL ABSTRACT



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ABSTRACT

We have conducted a comprehensive first-principles study of the tensile and fracture process of the TiN (111)/AlN(111) multilayered coatings with different thicknesses of AlN. We find that the ideal tensile strength of TiN/AlN systems is weakened with the increase of the thickness of AlN. A strikingly different fracture mode is identified for the coatings with differing thicknesses of AlN, that is, the fracture occurs in TiN for the coatings with one layer of AlN, while in the AlN for those with three or five layers of AlN. By applying several analytic methods, we attribute such difference to the variation in charge density and atomic hybridization, and demonstrate that charge transfer plays a key role in affecting mechanical properties of the coatings during a tensile process. The theoretical calculations presented here provide insight to atomic-scale effects of the thickness of AlN in complex TiN/AlN multilayered coatings that can be difficult to obtain by experiments alone but which are of practical significance for further understanding and improvement of such functional multilayered coatings.

1. Introduction

Multilayered coatings of transition metal nitrides have received considerable interest over the past decades, largely because their outstanding properties are important for many applications, including the extreme hardness and the good wear resistance. Controlling the microstructures and bonding at the interfaces is of significant importance for the performances and lifetime of coated tools [1–4]. Among the coatings, multilayered TiN/AlN ones, which are produced by alternating growth of the two host mononitrides, have attracted the broadest attention. The (Ti,Al)N nitride shows the FCC

* Corresponding author at: School of Manufacturing Science and Engineering, Sichuan University, Chengdu 400044, China. Tel.: +86 85402279; fax: +86 85405301.
** Corresponding author at: Advanced Institute for Materials Research, Tohoku University, 2-1-1 Katahira, Aoba-ku, Sendai 980-8577, Japan. Tel.: +81 222175931; fax: +81 222175930.
E-mail addresses: deqiang.yin@scu.edu.cn (D. Yin), zcwang@wpi-aimr.tohoku.ac.jp (Z. Wang).

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NaCl-type structure [5], and the $Ti_{1-x}Al_xN$ solid solution has been synthesized [6]. On the other hand, the AlN could have a couple of crystal structures: the stable wurtzite structure (w) with a hexagonal symmetry and two metastable phases with a cubic symmetry, B1 (labeled FCC with NaCl prototype) and B3 (ZnS prototype). Interestingly, these crystal structures can be tuned by controlling the thickness of AlN due to the template effect. For instance, the w-AlN can transform to FCC-AlN, forming a coherent interface with FCC-TiN when the thickness of AlN ranges from 0.5 to 2 nm. Such template effect has also been identified in multilayered coatings involving SiC [7], SiO_2 [8], Si_3N_4 [9], and AlON [10].

Because of high hardness, good wear and oxidation resistance, as well as multiple phases of AlN, the AlN/nitride multilayered coating has been the subject of intensive research owing to the hopes its raises for technological applications and also for its fundamental scientific significance, including the TiN/AlN [11–13], VN/AlN [14], NbN/AlN [15,16], and CrN/AlN [17–20]. Experimentally, Li et al. [21] reported that the AlN in the VC/AlN multilayers can be crystallized to a cubic structure when its layer thickness is less than 1 nm. As a consequence, the multilayers are grown coherently with significantly enhanced hardness (maximum of 40.1 GPa). On the other hand, Kim et al. [12–14] fabricated the epitaxial AlN/TiN(001) superlattices with the AlN layer thickness of not more than 2 nm, and demonstrated the formation of FCC-AlN when the AlN film is thin. Li et al. [22] also prepared a series of AlN/TiN multilayers with different modulation periods, and concluded that the coating reaches the highest hardness when the modulation period is 2 nm due to the alternative strain fields resulting from the coherent growth of FCC-AlN and TiN. Likewise, AlN in the AlN/CrN multilayered coating can exhibit the B1 structure with a high hardness of 40 GPa for the coating when the bilayer period is 3.8 nm [20]. Moreover, Wen et al. [15] recently deposited the NbN/AlN nano-multilayer films on Si(100) substrates by modulating the AlN thickness from 2.2 to 12.2 nm, and found that both the hexagonal wurtzite-AlN(0002) and FCC-AlN(111) are coherently bonded to the FCC-NbN(111). Moreover, the AlN thickness can determine coherency of the FCC-NbN(111)/w-AlN(0002) by minimizing the total energy and forming a strong fiber texture of NbN(111)/AlN(0002).

Theoretically, Chawla et al. [23] combined the finite element (FEM) and density functional theory (DFT) method to investigate the epitaxial stabilization of FCC-AlN layers in the TiN/AlN and CrN/AlN systems. They calculated the strain energy stored in the bulk and predicted that the (111) growth mode is energetically more favorable to stabilize the FCC-AlN than the (100). On the other hand, Chen et al. [11] applied the first-principles method to simulate the growth process of AlN thin film on TiN, and determined that the critical thickness of AlN is 1.95 nm. In addition, they also offered physical insights into the thickness-dependent structural transformation at the atomic scale. Moreover, Stampfl and Freeman [24] investigated structure and stability of rocksalt interfacial systems, AlN/VN, AlN/TiN and VN/TiN, and found that the systems are increasingly less stable with the increase of thickness owing to the lattice mismatch between the host nitrides.

All of these studies, albeit experimentally or theoretically, offer convincing evidence that the critical AlN thickness plays a key role in affecting mechanical properties of the AlN/nitrides multilayered coatings. Detailed knowledge on the role of AlN thickness in TiN/AlN multilayered coatings, particularly under the direct tensile process, is hence essential in elucidating the mechanism and controlling the performance of multilayered coatings. Here, we investigate, by first-principles calculations, how the AlN thickness can have an impact on the mechanical properties of TiN/AlN multilayered coatings. We have chosen purposely the TiN due to its good lattice match with AlN and also because it represents one of the most commonly used nitrides and could be coated onto many engineering materials.

2. Calculation detail and geometrical models

Calculations were performed using Cambridge Sequential Total Energy Package (CASTEP) within the framework of the DFT. Detailed calculation parameters were reported in the previous work [25]. We adopted cut-off energy of 600 eV and $12 \times 12 \times 12$ k-points for bulk TiN and FCC-AlN, which ensured the convergence of total energy to within 1–2 meV/atom. The strain–stress relationships were calculated by incrementally deforming the slabs along the applied strain. Both atomic basis vector orthogonal to the strain and the atoms in the slabs were allowed to relax at every step. To ensure a continuous strain, the starting atomic positions at each step were adopted from previous relaxed structures [26]. Initial models were fully optimized until the stress tensors turn sufficiently small ($\sigma < 0.2$ GPa). It should be noted that as an initial stage, the effect of defects on mechanical properties of multilayered coatings were neglected in this work. Since the epitaxial (111) texture are observed in the TiN/AlN multilayers [27,28], and the surface energy of (111) converges well by a 13-layer-thick slab [29], we have constructed the interfacial models consisting of one, three, and five AlN(111) layers sandwiched in two TiN (111) slabs of 13 layers, which are labeled 1L, 3L and 5L, respectively (Fig. 1). Namely, the TiN(111)/AlN(111)/TiN(111) sandwich system was applied. Moreover, periodic boundary of the TiN/AlN system was adopted with thickness of each TiN slab thicker than 13 layers. Lattice constants of AlN were elongated to match those of TiN to form coherent interfaces.

3. Results and discussions

3.1. Bulk properties and relaxed structures

We first verified the accuracy of computational methods by calculating bulk properties of both the TiN and FCC-AlN. With the

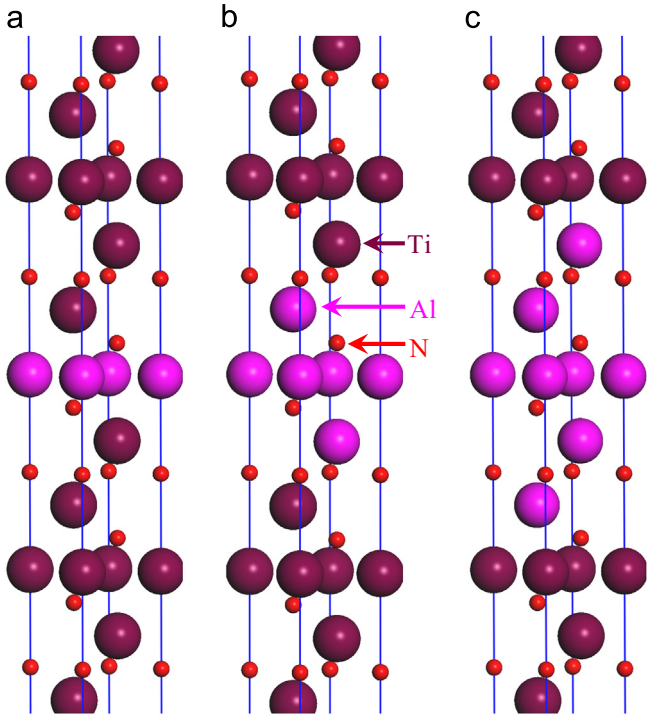

Fig. 1. Schematic plots of the TiAlN models: (a) 1L, (b) 3L, and (c) 5L. The view direction is close to [1$\bar{1}$0]. The top and bottom portions of the interface have been omitted.