Acta Materialia 127 (2017) 124–132

Contents lists available at ScienceDirect

Acta Materialia

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

Full length article

Systematic *ab initio* investigation of the elastic modulus in quaternary transition metal nitride alloys and their coherent multilayers

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ARTICLE INFO

Article history:
Received 9 November 2016
Received in revised form
21 December 2016
Accepted 8 January 2017
Available online 10 January 2017

Keywords:
Ab initio calculations
Elastic properties
Transition metal nitride alloys
Multicomponent
Multilayers

ABSTRACT

We give a comprehensive overview of the elastic properties of cubic quaternary transition metal nitride alloys and coherent nitride multilayers for design of wear resistant hard coatings. The elastic stiffness constants of the alloys are calculated using the special quasirandom structure method. For multilayers with sharp interfaces we prove the applicability of a linear-elasticity approximation and show that it can be used with success instead of performing direct computationally demanding *ab initio* calculations. We explore the trends and the potential of multicomponent alloying in engineering the strength and ductility of both, quaternary alloys and their multilayers. We investigate $X_{(1-x-y)}Ti_xAl_yN$ alloys where X is Zr, Hf, V, Nb or Ta, and present an analysis based on increasing *x*. We show that with increasing Ti content ductility can increase in each alloy. Elastic isotropy is observed only in $(Zr,Hf,V)_{(1-x-y)}Ti_xAl_yN$ alloys in the middle of the compositional triangle, otherwise a high Young's modulus is observed along [001]. We predict that coherent $TiN/X_{(1-x-y)}Ti_xAl_yN$ and $ZrN/X_{(1-x-y)}Ti_xAl_yN$ alloy multilayers with the [111] interfacial direction show increasing ductility with increasing *x*, while the multilayers with the [001] orientation become more brittle. We show that the Young's moduli variation in the parent bulk quaternary nitride alloy provide a reliable descriptor to screen the Young's modulus of coherent multilayers in high-throughput calculations.

1. Introduction

Non-equilibrium materials, such as metastable alloys, have unique properties that are utilized in modern industrial applications. Computational materials science offers an effective approach to tailor explore the potential of such materials. The efficiency of a computational screening is affected by the appropriateness of the applied physics models, as well as a coupling to a 'high-level' physical concept that is defined in hands with the complex technological needs. Based on the enormous success of computational materials science, numerous systematic computational studies have been devoted to develop and validate such concepts [1,2]. The elastic Young's modulus is a measurable material property that has been used in combinatorial high-throughput methods to select thin polymer films [3] or charting the elastic properties of inorganic compounds [4].

Metastable thin film cubic (NaCl-type) B1 $Ti_{(1-x)}Al_xN$ alloys are used as protective coatings in the cutting tools industry because of the material's excellent mechanical properties and oxidation resistance at elevated temperatures [5,6]. Cubic solid solutions can be deposited up to an Al content of 70 atomic % [7,8]. The thermodynamics of the material has been successfully described using sophisticated computational approaches [9–11]. The elastic properties of $Ti_{(1-x)}Al_xN$ [12–14], $Cr_{(1-x)}Al_xN$ [15] and textured $Zr_{(1-x)}Al_xN$ [16] have been investigated and a general symmetry based projection technique has been suggested for predicting the elastic tensor of alloys [13]. The kinetics of the (spinodal) decomposition of $Ti_{(1-x)}Al_xN$ has been simulated by solving the *ab inito* parameterized Cahn-Hilliard equation [17] and the importance of elastic anisotropy in the microstructure evolution has been established. Since anisotropic microstructure hinders the dislocation

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http://dx.doi.org/10.1016/j.actamat.2017.01.017
1359-6454/

motion through the material, microstructural design has became a strategic approach in developing hard coatings [18]. For example, superhard self-organized ZrAlN nanolabyrinthine [19] and Zr-Si-N nanocomposites [20] have been investigated by electron microscopy and nanoindentation. That is, in transition metal nitride alloys, elastic anisotropy is proved to be related to material hardness through the materials anisotropic microstructure [12,17,21,22].

The concept of multicomponent alloying in hard coatings to improve the materials hardness and thermal stability has been introduced by considering a mixing of CrN and $Ti_{(1-x)}Al_xN$ [23,24]. The basic idea of the concept consists of employing the spinodal decomposition to promote the formation of a metastable cubic phase of $Cr_{(1-x)}Al_xN$. It further underlines the increased interest for metastable phases in nitrides alloys. The zero temperature thermodynamics of quaternary transition metal nitride alloys has been recently investigated by Holec [25]. Though, cubic VN is found dynamically unstable at 0 K [26] the renormalized VN phonon dispersion relations calculated by Mei et al. [27] shows that the elastic constants do not change with the temperature. Since similar level of instability is assumed for NbN and TaN, calculations of the elastic constants at T = 0 K are highly valuable. The high temperature elasticity in TiN [28], CrN [29] and $Ti_{(1-x)}Al_xN$ [14] alloy has been investigated. However, the potential of multicomponent alloying for engineering the materials strength and elastic anisotropy in quaternary alloys has not been discussed yet.

Forming coherent multilayers, such as TiN/V(Nb)N or TiHfN/CrN, is proposed as alternative concept to extend the wear resistance and hardness of bulk monolithic materials, see Ref. [30]. The mixing thermodynamics of TiN/$Ti_{(1-x)}Al_xN$(001) compared with the one of $Ti_{(1-x)}Al_xN$ has recently been investigated experimentally [31,32] and by *ab initio* calculations [33]. Though electron microscopy and atom probe tomography combined with phase field simulations have predicted the occurrence of surface directed spinodal decomposition [17], it has been found less developed than the bulk-like spinodal decomposition in $Ti_{(1-x)}Al_xN$. During the coherent spinodal decomposition of the alloys, the microstructure can be approximated by local coherent multilayers with different interfacial orientations. Therefore, by predicting the Young's modulus of the multilayers one elaborates the material's local strength distribution which affects the microstructural evolution, and by that the hardness of the material.

This paper is organized as follows. Section 2 is devoted to the computational details and the methodology for calculating elastic stiffness constants of alloys and superlattices of alloys. In Section 3 we present the equilibrium structural parameters of the alloys. Thereafter, the elasticity of quaternary transition metal nitride alloys is discussed. Using increased Ti content we discuss the trends in altering ductility via multicomponent alloying. In the last subsection we investigate the strength (Young's modulus) of multilayers and establish the usage of the bulk alloy Young's modulus values to design wear resistant superlattices using high-throughput screening. Finally, a summary of our work is given in Section 4.

2. Methodology

2.1. Calculation details

Binary nitrides - AlN, TiN and XN, where X = Zr, Hf, V, Nb, Ta, together with their $X_{0.5}Al_{0.5}N$ and $X_{0.5}Ti_{0.5}N$ ternary alloys were modeled with $(4 \times 4 \times 3)$ supercells of 96 atoms. The supercell size was chosen based on the results in Ref. [13] and based on the unit cell of the cubic B1 lattice. The substitutional alloying was modeled using the special quasirandom supercell (SQS) approach by Zunger [34] with minimizing the Warren-Cowley pair short-range order (SRO) [35] parameters up to the seventh nearest neighboring shell in the metal sublattice. $X_{0.33}Ti_{0.33}Al_{0.33}N$ quaternary alloys were simulated by $(3 \times 3 \times 3)$ supercells similarly on the basis of B1 conventional cell with 216 atoms. The total energy calculations were performed within density functional theory (DFT) using the projector augmented wave (PAW) [36] approach implemented in the Vienna Ab initio Simulation Package (VASP) [37]. The exchange-correlation energy was approximated by the Perdew-Burke-Ernzerhof generalized gradient functional (PBE-GGA) [38]. The lattice parameters and all the internal atomic coordinates were relaxed to obtain the ground-state structure. In the elastic constant calculations we applied a plane-wave cutoff energy of 600 eV. The reciprocal-space integration was performed using the Monkhorst-Pack scheme [39] with a *k*-mesh of $(6 \times 6 \times 6)$ except for Nb and Ta related alloys where $(7 \times 7 \times 7)$ was applied.

The TiN/$Ti_{(1-x)}Al_xN$(001) multilayers were modeled with sharp interfaces using 1:1 materials ratio and 216 metal atoms all together. The models were more detailed explained in Ref. [40]. The elastic constants were calculated with a plane-wave cutoff of 520 eV and a Monkhorst-Pack *k*-mesh of $(5 \times 5 \times 3)$.

2.2. Elastic constants

The elastic stiffness constants

$$C_{ij} = \frac{1}{V_0}\frac{\partial^2 E(\vec{\varepsilon})}{\partial\varepsilon_i \partial\varepsilon_j}\bigg|_{\text{relaxed}} \tag{1}$$

using Voigt notation were extracted through the Taylor expansion of the total energy with respect to lattice distortion [41,42]. We applied strains $\vec{\varepsilon} = \{\varepsilon_1, \ldots, \varepsilon_6\}$ corresponding to ±1% and ±2% lattice distortions of the fully relaxed supercells without volume conservation. $E(\vec{\varepsilon})$ is the total energy of the distorted supercell and V_0 denotes the equilibrium volume of the non-distorted supercell.

The SQS approach in principle breaks the point group symmetry of the alloy and the different supercell models break it in different order. Therefore, inhomogeneous materials quantities of alloys, such as the elastic tensor in Eq. (1), have to be calculated carefully [40]. Recently, a symmetry based projection technique [43,44] has been suggested to derive accurate prediction of the elastic and piezoelectric tensor of substitutional alloys [13,45]. The symmetry projected cubic stiffness constant are calculated as

$$\overline{C}_{11} = \frac{C_{11}+C_{22}+C_{33}}{3}, \overline{C}_{12} = \frac{C_{12}+C_{13}+C_{23}}{3},$$
$$\overline{C}_{44} = \frac{C_{44}+C_{55}+C_{66}}{3} \tag{2}$$

based on nine independent tensor elements: $C_{11}, C_{22}, C_{33}, C_{23}, C_{13}, C_{12}, C_{44}, C_{55}$ and C_{66}. The mechanical stability of a cubic crystal is proved by fulfilling the Born stability criteria [46];

$$\overline{C}_{44} > 0,\ \ \overline{C}_{11} > |\overline{C}_{12}|,\ \ \overline{C}_{11} + 2\overline{C}_{12} > 0. \tag{3}$$

Elastic anisotropy of single crystals can be quantified either by Zener's anisotropy ratio $(\overline{A} = 2\overline{C}_{44}/(\overline{C}_{11} - \overline{C}_{12}))$ or by the directional dependence of the Young's modulus [41] which in cubic crystals is written as

$$\frac{1}{\overline{E}_{\ell_1\ell_2\ell_3}} = \overline{S}_{11} - 2\left(\overline{S}_{11} - \overline{S}_{12} - \frac{1}{2}\overline{S}_{44}\right)\left(\ell_1^2\ell_2^2 + \ell_2^2\ell_3^2 + \ell_1^2\ell_3^2\right). \tag{4}$$

here, $\overline{S}_{ij}$ is the elastic compliance coefficients which is the inverse of