Surface & Coatings Technology 286 (2016) 178–190

Contents lists available at ScienceDirect

Surface & Coatings Technology

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

Recent progress and new directions in density functional theory based design of hard coatings

Denis Music *, Richard W. Geyer, Jochen M. Schneider

Materials Chemistry, RWTH Aachen University, Kopernikusstr. 10, D-52074 Aachen, Germany

ARTICLE INFO

Article history:
Received 27 October 2015
Revised 4 December 2015
Accepted in revised form 11 December 2015
Available online 12 December 2015

Keywords:
Hard coatings
Diamond-like carbon
TiAlN
Density functional theory

ABSTRACT

Hardness, one key property of hard coatings, is proportional to shear modulus, which can be predicted using density functional theory (DFT). Besides considering hardness, a design methodology for hard coatings must include additional physical and chemical properties, such as thermal conductivity. Recently, also the hard coating–environment (or workpiece) and hard coating–substrate interfaces have been described, constituting new research directions. We have reviewed two commercially successful benchmark hard coatings from the DFT perspective: (i) amorphous diamond-like carbon (DLC) and (ii) metastable TiAlN. Major DFT contributions to the DLC research are the correlation between density and electronic structure as well as identification of reaction products formed during atmospheric exposure to be the main cause for low friction at elevated temperatures. In the case of TiAlN based hard coatings, DFT enabled atomic scale understanding of the phase stability, formation of defect structures and interfaces for the elastic properties, enhancement of toughness, initial stages of oxidation, and interaction with molten polymers and metals. Future DFT design challenges include broader high-throughput screening, additional properties, nucleation and growth phenomena, and multiple interfaces.

© 2015 Elsevier B.V. All rights reserved.

Contents

1. Introduction

Hardness can be conceived as resistance of materials to propagation of dislocations and is hence defined by bond strength and underlying deformation mechanisms. Evidently, a major design criterion for hard coatings is hardness [1]. The hardest known material in nature is diamond, which exhibits strong, short, and directional bonds [1]. Thus, covalently bonded compounds with short bonds are good candidates for hard coatings. Usually, compounds made of light elements (boron, carbon, nitrogen, and oxygen) are considered in this case [1]. For instance, cubic BN is isoelectronic to C and hence a good hard coating [2]. Another class of hard coatings are partially ionic compounds composed of transition metals and light elements [1]. A typical example of this class is TiB_2 [3].

Besides considering hardness, a design of hard coatings must include quite many other features. Additional physical and chemical properties may be of relevance when hard coatings are multifunctional, which is often the case in high-tech applications. For instance, the optical properties of hard coatings are relevant for protection of optical storage devices [4]. Some properties may be self-excluding, complicating the design of hard coatings. Furthermore, many thermal properties, such as thermal stability and thermal conductivity, are detrimental for hard coatings [5]. Coatings lacking thermal stability may undergo phase transitions which may be accompanied by volume changes [6], causing cohesive and/or adhesive failure. Furthermore, careful analysis and adjustment of the thermal conductivity is also relevant for protecting

* Corresponding author.
E-mail address: music@mch.rwth-aachen.de (D. Music).

http://dx.doi.org/10.1016/j.surfcoat.2015.12.021
0257-8972/© 2015 Elsevier B.V. All rights reserved.

the tool (substrate) from the heat developed during the application or more uniform distribution of dissipated heat through the coating [7]. A very important aspect of hard coating design is the treatment of interfaces, i.e. hard coating–environment (or workpiece) and hard coating–substrate interfaces [5]. Furthermore, thermal expansion misfit between the hard coating and the substrate gives rise to thermal stresses in the coating.

In the 1980's, a typical strategy to discover new hard coatings driven by more and more demanding cutting edge applications was based on models and experimentally determined rules, such as the correlation between bulk modulus and chemical bonding to gauge hardness, which was introduced by Cohen [8], the Hägg rule to select elements stabilizing a desired structure [9], the Hall–Petch relationship to select a suitable grain size (microstructure) [10,11], and the Movchan and Demchishin [12] as well as Thornton structure-zone model to associate processing parameters and microstructure [13]. The key research question in the 1980's was to relate microstructure and hardness on the basis of grain size, grain and column boundary structure, phase and atomic distribution, impurity control, and texture, so as to facilitate hard coatings with extreme hardness and possibly some level of toughness, which appears to be self-excluding [14]. Based on these models and rules as well as large empirical efforts facilitated through high resolution analytics, such as transmission electron microscopy, exciting and pioneering achievements were made in the 1980's, including metastable compounds, e.g. TiAlN [15], and artificial structures, e.g. superlattices and other nanocomposites [16–18]. Even though these models and rules are more efficient than simple trial-and-error approaches, they soon reached their limits. For instance, a bond length is a typical parameter in some of these models. However, how could one know it a priori when designing a completely new hard coating or even a metastable (and/or nanostructured) hard coating?

Despite the fact that density functional theory (DFT) [19] was developed in the 1960's, it remained dormant for the field of hard coatings until the 1990's when computers were advanced enough to tackle some of the questions raised by the hard coating community. Its major strength is that it provides correlations between composition, structure, and properties without any empirical parameters. Hardness is governed in part by the electronic structure. This is especially the case for single-crystal lattices [20]. Thus, it is expected that electronic structure theories, for example DFT, can provide fundamental insights. However, for complex microstructures, hardness is strongly dependent on the resistance to plastic deformation, e.g. dislocation glide, grain sliding, and grain rotation. To describe these deformation mechanisms, active at size scales often not easily accessible to computationally-demanding DFT calculations, scale hopping [21] and/or scale bridging [22,23] are meaningful research strategies. In the 1990's bulk modulus data were correlated with the electronic structure for ideal, defect free, structures [24,25]. To design long-sought tough hard coatings, the Pugh notion [26] has sometimes been utilized, which provides a crystal structure dependent classification scheme for materials behaving brittle or ductile. For instance, the bulk to shear modulus ratio gauging the brittle/ductile crossover in metallic glasses [27] is different from the value observed for body-centered cubic, face centered cubic, and hexagonal crystals, as originally proposed by Pugh [26]. However, applying this notion to arbitrary crystal structures can result in misinterpretations. This perhaps fuels the discomfort experienced by some experimentalists towards the relevance of DFT predictions for engineering applications. This may be overcome by communicating the shortcomings inherent in the approximations employed. The challenging prediction of toughness and the plastic behavior by DFT has been undertaken since the 1990's. The price of computers has dropped drastically over the years. In the beginning of the 21st century, a price reduction of about 20% per year resulted in a much increased availability of computational resources, which enabled more complex and systematic DFT studies. Also, hard coatings were systematically investigated, where examples include the exploration of valence electron concentration – phase stability and valence electron concentration – elastic property correlations. For instance, tuning the phase stability of transition metal carbides to enable design of multilayer hard coatings [28] and stabilization of super-hard fluorite RuO_2 by alloying with transition metals and nonmetals [29] were carried out. Furthermore, valence electron concentration – elasticity correlations were also systematically explored in the first decade of this century, e.g. considering early transition metal carbides and nitrides [30] and Ti–Al phases [31]. These systematic studies at first included only several configurations, which have lately been extended to probing all competitive phases, such as nanolaminated $M_{n+1}AlX_n$ (M = Sc, Ti, V, Cr, Mn; X = C, N; n = 1–3) with all binary and ternary counterparts, enabling beneficial input for experiments [32]. High-throughput screening DFT based algorithms for designing of hard coatings are the logical consequence of this trend [33].

It is known that shear modulus scales with hardness, better than bulk modulus does [34,35], which is where DFT is very beneficial. By calculating all elastic constants, both polycrystalline and orientation-dependent shear moduli can be obtained [36]. One needs to bear in mind that DFT is computationally expensive so that many approximations are introduced (see below) as well as simplifications (ideal crystals, 0 K, etc.). Still, often elastic constants are predicted within 10% (max. 20%) deviations from the measured ones [37]. It must be noted that DFT does not only provide numerical predictions, it also aids on uncovering the physical and/or chemical origin of e.g. enhanced hardness [35], stiffness [38–40], phase stability [28,41], and other relevant properties. There are also approaches to calculate intrinsic hardness [42] and ideal stress–strain curves [43] as well as to describe ideal cleavage [44]. Often, defect-free crystals without appropriate morphological features and/or defects are considered. Explicitly including defects (e.g. point defects, extensive defects such as grain boundaries) into DFT studies is possible, but requires enormous computational time. These efforts are being made recently (see below).

Besides explicitly including defects, new DFT research directions in the field of hard coatings include the treatment of hard coating–environment (or workpiece) and hard coating–substrate interfaces [5]. These aspects have only recently been considered due to computational resources (see Fig. 1 for an example in which hard coating Mo_2BC [45] reacts with environment [46] and a workpiece [47]). Furthermore, the hard coating needs to adhere to the substrate, which can be tackled by e.g. calculating the work of separation [48]. DFT can also provide valuable predictions on thermal expansion of these individual counterparts based on phonons [49] or molecular dynamics [50], but still hard coating–substrate interfaces are challenging to consider due to large number of atoms required to describe them.

Future challenges for the DFT based design of hard coatings include high-throughput screening, additional physical and chemical properties, nucleation and growth phenomena, and multiple interfaces. The high-throughput DFT based screening already is applied in some areas of physics, chemistry, and materials science [51], but broader application to hard coatings is still at its infancy. Some efforts have already started with ternary transition metal nitrides [33]. Alternatively, it is conceivable that required approximations may be developed to provide this fast screening [52,53]. Very commonly, thermal management is ignored in design of the hard coatings, as it is very demanding to handle not only from DFT perspective, but also from the perspective of precise measurements. For instance, thermal stresses develop due to thermal expansion misfit between the hard coating and the substrate. Heat conductivities are also of relevance. Many efforts have been done recently to facilitate design which includes the thermal management [54–57], but still much is left to be done. While growth phenomena of hard coatings have only been addressed recently [58,59], DFT based nucleation studies are still not available. Not only coating – environment and hard coating–substrate interfaces are important, but also there are very often even more complex interfaces present, such as oxidized hard coating–workpiece interface [46], tissue phases in grain boundaries [17,60,61]. These aspects must be considered in a DFT design.

Download English Version:

https://daneshyari.com/en/article/1656775

Download Persian Version:

https://daneshyari.com/article/1656775

Daneshyari.com