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Characterization of multilayer nitride coatings by electron microscopy and modulus mapping

Sai Pramod Pemmasani[a, b], *Koteswararao V. Rajulapati*[b], *M. Ramakrishna*[a], *Krishna Valleti*[a], *Ravi C. Gundakaram*[a,*], *Shrikant V. Joshi*[a]

[a]*International Advanced Research Centre for Powder Metallurgy and New Materials (ARCI), Balapur P.O., Hyderabad — 500005 India*
[b]*School of Engineering Sciences and Technology, University of Hyderabad, Gachibowli, Hyderabad — 500046 India*

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ABSTRACT

This paper discusses multi-scale characterization of physical vapour deposited multilayer nitride coatings using a combination of electron microscopy and modulus mapping. Multilayer coatings with a triple layer structure based on TiAlN and nanocomposite nitrides with a nano-multilayered architecture were deposited by Cathodic arc deposition and detailed microstructural studies were carried out employing Energy Dispersive Spectroscopy, Electron Backscattered Diffraction, Focused Ion Beam and Cross sectional Transmission Electron Microscopy in order to identify the different phases and to study microstructural features of the various layers formed as a result of the deposition process. Modulus mapping was also performed to study the effect of varying composition on the moduli of the nano-multilayers within the triple layer coating by using a Scanning Probe Microscopy based technique. To the best of our knowledge, this is the first attempt on modulus mapping of cathodic arc deposited nitride multilayer coatings. This work demonstrates the application of Scanning Probe Microscopy based modulus mapping and electron microscopy for the study of coating properties and their relation to composition and microstructure.

1. Introduction

Physical vapour deposited (PVD) coatings on cutting and forming tools are known to enhance properties such as hardness, oxidation resistance and thermal stability [1]. The behaviour of a coating is directly related to its microstructure as well as crystal structure and constitution of different phases formed during the deposition process [2]. The use of multi-layer coatings, where each layer imparts a specific functionality to enhance the overall coating performance, is already prevalent in the industry, especially for cutting tool applications [3]. While nano-multilayer coatings, which consist of alternating layers with different compositions and thickness in the range of a few nm to ~100 nm, have shown enhanced toughness as a result of crack redirection, renucleation [4] and columnar shear sliding [5], nanocomposite coatings comprising nanocrystalline grains embedded in an amorphous matrix of another material have exhibited superhardness accompanied by superior oxidation and thermal resistance [6]. It has been reported that the hardness of nano-multilayer coatings is directly dependent on the bilayer period thickness [7] while the toughness of nano-composite coatings is dependent on the grain structure of the coating [8]. The phase and crystal structure are also known to influence coating properties such as hardness and toughness. For example, it has been reported that the Face Centred Cubic (FCC) NaCl type structure in case of TiAlN coatings leads to a higher hardness and modulus on account of the reduction in lattice parameter with increasing Al fraction [1,9,10] while the

* *Corresponding author*. Tel.: +91 40 24444047; fax: +91 40 24442699.
E-mail address: ravi.gundakaram@arci.res.in (R.C. Gundakaram).

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Hexagonal Close Packed (HCP) wurtzite type structure formed at Al fractions above 0.6 causes a drastic drop in hardness due to the disruption of the columnar grain structure [9,11] and an increase in the volume of voids at grain boundaries [11].

While multi-layer coatings have been extensively developed by Chemical Vapour Deposition (CVD) techniques [12], few research publications on new generation PVD multi-layer coatings are available, although some patents exist[13,14]. The new generation PVD coatings involve multiple layers comprising both nanocomposite and conventional layers, each layer being tailored to discharge a specific function to enhance the durability and performance of the overall coating [15,16]. Increased performance has been reported for a number of double layer systems [12]. The use of Ti or TiN interlayers has been widely reported to improve adhesion [1,3] and adhesive interlayers such as Cr/CrN on tools have been reported to improve tool life [17]. Recently, a multilayer coating with a three layer design comprising an adhesive underlayer of TiN/Ti, an intermediate ceramic layer with 90% Al_2O_3 and 10% AlN, and a wear resistant top layer that consists of TiAlCrN nanoscale-multilayers was reported to enhance tool life by about 2.5–8 times when compared to standard coated tools [18].

Notwithstanding the above efforts, no detailed report exists on the role of microstructure in such new generation triple layer coatings. The use of microscopy, both electron and scanning probe, has found many applications especially in the characterization of both single layer and multilayer nitride coatings [19–21] while modulus mapping is relatively unexplored for the study of hard coatings. The design of materials with a graded modulus has been reported to enhance strength and toughness as seen in functionally graded coatings [22] and also in many natural materials [23] where the low modulus region is reported to accommodate stress damage and, thereby, prevent or slow down crack propagation. In the present study, triple layer coatings are studied which comprise of multilayers that are intended to possess alternating high and low moduli. Such a structure should enable enhanced crack resistance in these coatings. The generation of modulus maps will thus be vital to the validation of the coating design and the deposition sequence. The coatings are characterized using a combination of Scanning Electron Microscopy (SEM) based micro-diffraction, Focused Ion Beam (FIB), Transmission Electron Microscopy (TEM) and Scanning Probe Microscopy (SPM) techniques that cumulatively enable a comprehensive investigation. Multi-scale characterization was carried out where the preliminary coating thickness was inferred from optical microscopy, while more accurate measurements were done in the SEM and FIB, with the latter enabling a detailed observation of the multilayer coating cross section and the various layers. TEM permitted identification of the nano-layered structure of the multilayers apart from providing phase information through Selected Area Electron Diffraction (SAED). Electron Backscattered Diffraction (EBSD) provides a simple method for determination of phase in addition to providing information on grain structure and orientation. However, EBSD has not been extensively used for the study of PVD coatings. SPM based techniques can provide detailed information on the coating properties such as modulus and stiffness in addition to providing near atomic resolution for the study of topographic details. Stiffness maps of coatings obtained by ultrasonic force microscopy have been used to detect nanoscale elastic inhomogeneities in case of TiN [24]. To the best of our knowledge, no previous study exists on the modulus mapping of multilayer nitride coatings by an SPM based technique. Such a comprehensive study of the microstructure and phase constitution at multiple length scales, complemented by evaluation of coating properties such as modulus and stiffness, would be invaluable in arriving at microstructure–property correlations to understand coating behaviour and enhance performance.

2. Experimental

2.1. Synthesis

Three triple layer coatings of thicknesses 2, 4 and 7 μm were prepared (designated ML1, ML2 and ML3, respectively) in a Platit π^{300} Cathodic Arc deposition System with two sets of cathodes — a 67Al–33Ti Central Rotating Cathode and Cr, 82Al–18Si and Ti Lateral Rotating Cathodes [25]. Coatings were deposited on high speed steel (HSS) substrates of size — 12.5 × 12.5 × 5 mm. The coatings were deposited employing a bias voltage of −50 V, a substrate temperature of 450 °C and a nitrogen partial pressure of 4.5×10^{-2} mbar. The coating architecture is based on a similar design developed by Platit [15]. The schematic of the triple layer coatings used in the present study is illustrated in Fig. 1. A typical design of the triple layer coating deposited involves a TiN–TiCrN underlayer on a tool steel substrate followed by a thick TiAlN layer with a gradient layer in between. The gradient layer comprises a varying concentration of the elements Ti, Al and Cr in order to allow for a smooth transition between different layers and for accommodation of the cathode power ramp-up and ramp-down between deposition steps. The TiAlN layer is followed by another gradient layer over which nano-multilayers of Ti–Al–Cr–Si–N are deposited. The Ti–Al–Cr–Si–N nano-multilayers are designed to have alternating high and low Si and Cr compositions with a low Si % accompanied by a high Cr % and vice-versa. The role of Si in TiAlCrSiN is to promote the formation of a nanocomposite structure, where amorphous Si_3N_4 is formed

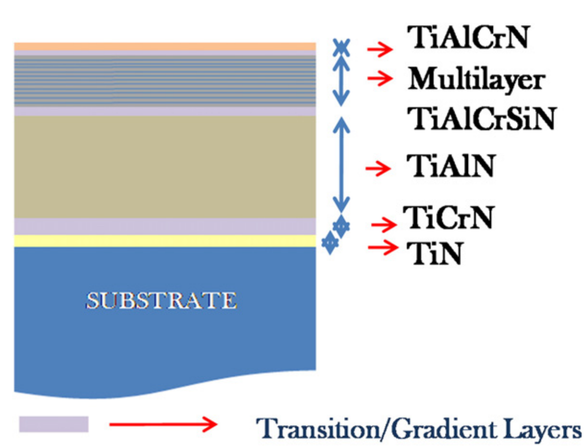

Fig. 1 – Schematic of the multilayer coating with the triple layer structure.