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Extremely hard, damage-tolerant ceramic coatings with functionally graded, periodically varying architecture

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Abstract

Functionally graded, multilayer coatings consisting of alternating TiN/TiSiN layers were synthesized in an attempt to overcome the innate brittleness of TiSiN nanocomposite coatings, whilst maintaining high hardness. These coatings exhibited key structural characteristics that are known to render many naturally occurring materials extremely hard and robust. Transmission electron microscopy revealed that shear sliding of columnar TiN grains played a vital role in controlling the inelastic deformation of these coatings, conferring a greater resistance to contact damage. Moreover, nanoindentation experiments showed that the multilayer coatings exhibited high hardness, attributed to the strong shear resistance offered by the hard TiSiN layers. A dependence of coating hardness upon indentation penetration depth (h_t) was found to be proportional to $1/\sqrt{h_t}$, according to a mechanistically based model, from which the shear stress was determined. The energy dissipation during indentation was also quantified to show the critical role of the shear stress, regulated by the thickness of TiSiN layers, in resisting contact damage in the coatings. Finite-element models were constructed and the presence of transgranular cracks in the monolithic TiSiN coating was clarified based upon experimental observations. Furthermore, the simulations revealed that the transition of the dominant deformation mechanism from brittle transgranular cracking to intergranular shear sliding was controlled by the microstructural characteristics of the coatings. Enabled by the shear sliding, as well as periodic changes in elastic modulus, such a functionally graded multilayer structure was effective in lowering the magnitude and extent of stress concentrations, thereby extending the damage tolerance accessible to a ceramic coating.

Keywords: Physical vapor deposition (PVD); Multilayers; Nanoindentation; Deformation structure; Finite-element analysis

1. Introduction

Ceramic coatings are applied to enhance performance and extend the service life of metallic components used in applications ranging from machining and transportation to bioengineering. Considerable effort has been made to improve the mechanical properties of these coatings; recently, superhard coatings (i.e. hardness >40 GPa) have been developed. Among them, TiSiN coatings, consisting of TiN nanocrystals held together by a thin strong covalent SiN_x layer [1,2], have attracted considerable attention; grain size, interlayer thickness and composition have been identified as key factors that control the hardness of these coatings [3–8]. For example, the critical thickness of SiN_x interfacial layer and its role in determining the hardness of the TiSiN can be explained in terms of valence charge transfer from the metallic TiN to the interlayer [7,8]. Veprek and co-workers reported that ultra-high-hardness (∼100 GPa) TiSiN could be obtained [1,3] if the TiN nanocrystals are separated by one monolayer of Si_3N_4.

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Unfortunately, such coatings can only be synthesized under extreme high vacuum and under precisely controlled deposition conditions. For instance, a mere 0.3% oxygen contamination can dramatically reduce the hardness of TiSiN from >100 to ~35 GPa [1]. The critical conditions required for synthesizing the ultra-high-hardness TiSiN coatings would render processing prohibitively costly, if not impossible, for industrial applications. Nevertheless, TiSiN coatings are inherently brittle and often deform in a catastrophic manner under mechanical loading [9,10], which has limited their applications. Innovative design strategies are therefore needed to provide a more economical and practical path to obtaining a hard, yet damage-tolerant, coating that deforms in a predictable manner during operation.

Interestingly, many naturally occurring materials exhibit an unusual combination of extraordinary strength and damage resistance [11–15]. These materials often exhibit a microstructure consisting of functionally graded, alternating layers of mineral and protein phases [16]. Such a configuration can accommodate deformation through the shear sliding of the mineral platelets. In doing so, contact damage can be avoided and structural integrity maintained [17]. The structural characteristics of these natural materials have recently inspired the design and synthesis of high-performance bulk materials [18]. For example, novel Al_2O_3/poly(methyl methacrylate) hybrid materials based on the multilayered structure of nacre were prepared, with strengths comparable to pure alumina, but with fracture toughness values an order of magnitude larger [19].

TiN coatings prepared by physical vapor deposition (PVD) typically exhibit a columnar-grained structure [20]. Intergranular shear sliding often occurs during loading, preventing brittle failure, but often at the expense of hardness [20–22]. Inspired by material design principles exhibited by natural materials, ceramic coatings that have a multilayered structure consisting of TiN layers, alternated by thin, extremely hard TiSiN layers, were synthesized in this work. They serve as a prototype to test the hypothesis that a unique combination of high strength and damage tolerance can be imparted to ceramic coatings through microstructural tailoring. Cross-sectional transmission electron microscopy (TEM) was used to characterize the resulting microstructures and ascertain the mechanisms that underpin the deformation of these coatings. Based upon these experimental observations, mechanistically based models were constructed to understand the critical roles of microscopic architecture for enhancing the mechanical properties of these ceramic coatings. In addition, finite-element analyses were carried out to predict the occurrence of cracks in the coatings and to gain a better understanding of the brittle–ductile transition in relation to the coating microstructure. Furthermore, numerical modelling was used to reveal the origins of the strength and toughness attained from this bio-inspired multilayer combination and to quantify the contribution of various mechanisms (such as gradient design, modulus values and shear sliding) to the damage tolerance of these newly developed multilayer coatings.

2. Experimental

2.1. Sample preparation

AISI M42 tool steel substrates were polished to a surface roughness, R_a, of ~0.02 μm and four coatings were deposited by using a closed-field unbalanced magnetron sputtering ion-plating system (UDP650, Teer Coatings Ltd., UK). Prior to deposition, the chamber was pumped down to a background pressure of $<2.0 \times 10^{-6}$ Torr (2.6×10^{-4} Pa). The surfaces of the substrates were sputter cleaned with an Ar plasma for 30 min at a bias voltage of −500 V to remove oxides and other contaminants on the substrates. Four elemental targets (i.e. three Ti and one Si) were used. During deposition, both argon working gas and nitrogen reactive gas (99.995% purity) were introduced continuously into the chamber, and the total gas pressure ($Ar + N_2$) maintained at 1.3×10^{-3} Torr (0.17 Pa) to form nitrides. The concentration of nitrogen was controlled using a piezoelectric valve, which was regulated dynamically by the signal fed from an optical emission monitor. The temperature of the substrates was kept at ~550 °C by a heater, and they were mounted on a turntable holder rotating at a speed of 10 rpm. The target-to-substrate distance was 17 cm. A Ti wetting layer (~0.2 μm), a TiN transition layer (~0.5 μm) and a compositionally graded TiSiN layer (~0.3 μm) with increasing Si content were deposited. The graded layer was achieved by linearly increasing the current applied to the Si target from 0 A to 2.5 A. Subsequently, 10 bilayer periods, each consisting of a TiSiN and a TiN sublayer, were deposited to form a TiSiN/ TiN multilayer structure, with the TiSiN being the outermost layer (Fig. 1). The bilayer period in these coatings was ~200 nm thick. Constant target currents of $I_{Ti} = 8$ A and $I_{Si} = 2.5$ A were used to deposit the TiSiN sublayers. When creating the TiN sublayers, no current was applied to the Si target. The bias voltage was kept at −60 V throughout the deposition process. The deposition rates for the TiN and TiSiN layers were ~14.7 and ~16.5 nm min^{-1}, respectively. The thickness of each

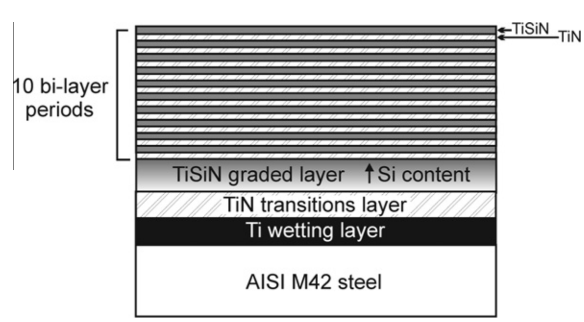

Fig. 1. Schematic diagram showing the architecture of the coatings studied.