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Investigation of $Ti_{0.54}Al_{0.46}/Ti_{0.54}Al_{0.46}N$ multilayer films deposited by reactive gas pulsing process by nano-indentation and electron energy-loss spectroscopy

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ABSTRACT

Physical vapour deposition technology is well suited to the deposition of advanced TiAlN-based coatings. Among these thin films, multilayer systems consisting of stacked layers of metallic $Ti_{1-x}Al_x$ and nitride $Ti_{1-x}Al_xN$ with x around 0.5 are expected to have improved mechanical properties with respect to single nitride layers of the same composition. A set of $Ti_{0.54}Al_{0.46}/Ti_{0.54}Al_{0.46}N$ multilayer films with five different periods Λ (from 4 to 50 nm) were deposited using the reactive gas pulsing process (RGPP). This RGPP approach allows the deposition of TiAl-based alloy/nitride multilayer films by radio frequency reactive magnetron sputtering with a controlled pulsing flow rate of the nitrogen reactive gas. The coherent growth of the multilayer coatings, depending on the period, is checked by X-ray diffraction and the mechanical properties are determined by Berkovich nano-indentation and friction experiments. A model to describe the dependence of the indentation modulus M and the hardness H_B on the penetration depth h, the period Λ, and the film thickness e_f is proposed. The indentation modulus of the multilayer films (M at h = 0 and for $e_f \sim 1900$ nm) is found to be in the range of 340 GPa < M < 525 GPa ≈ M($Ti_{0.54}Al_{0.46}N$). For a fixed penetration depth, M follows a Hall and Petch evolution as a function of the period ($4 \le \Lambda \le 50$ nm). The Berkovich hardness, 25 GPa < H_B < 50 GPa, also presents the same kind of evolution, and for Λ < 16 nm (at h = 0), $H_B > H_B$ ($Ti_{0.54}Al_{0.46}N$) = 33 GPa. Hence, a superlattice effect is clearly evidenced. Moreover, for the larger periods, the wear behaviour of these multilayered coatings seems to be dominated by the plastic deformation of the metallic layer. The multilayer coating of period Λ = 10 nm, which exhibits a diffraction pattern typical of superlattices and favourable mechanical properties, is more precisely investigated. Transmission electron microscopy confirms the main growth of the film along the [111] direction, and the evolution of the bonding of nitrogen in the direction normal to the rough interfaces between $Ti_{0.54}Al_{0.46}$ and $Ti_{0.54}Al_{0.46}N$ layers is specified by electron energy-loss near-edge spectroscopy. Nitride nano-grains are included in the metallic layer, which attests to the mixing of nitrogen into the layers. The structure of these nano-grains presents a progressive evolution into the layer and gradually acquires a TiN-like structure near the interface. For this Λ = 10 nm period, the indentation modulus and hardness for different penetration depths are weakly sensitive to the multilayer film thickness.

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1. Introduction

Metal nitride coatings such as titanium and aluminium nitride films have attracted considerable interest because of their physical and chemical properties such as oxidation resistance and excellent mechanical performances due to their high hardness, toughness, and wear resistance [1]. They are extensively used in industry and particularly in machining applications as protective coatings of cutting tools [2]. $Ti_{1-x}Al_xN$ can be considered as a ternary nitride model system in which the crystallographic structure evolves from the face centered cubic (fcc) NaCl lattice for low Al contents to the hexagonal wurtzite-type (hcp) for high Al contents. Although AlN is poorly soluble in TiN, the reactive sputtering from a TiAl metallic target allows the deposition of coatings in which Al atoms are partially substituted for Ti [3,4]. The best mechanical properties are obtained when the maximum Al content is substituted for Ti in the fcc lattice [5,6]. For as-deposited coatings, which exhibit columnar microstructure, the indentation modulus M and the Berkovich hardness H_B values are strongly dependent on the composition of $Ti_{1-x}Al_xN$, and a transition occurs when both fcc and hcp phases grow in the film [3,7]. The best

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mechanical properties – high hardness and wear resistance – are observed for films whose Al content is around 50 at.% of the metallic part.

Various attempts to improve the performances of hard coatings have been carried out. One way consists in depositing TiAlN-based multilayer coatings in order to combine different properties. The large number of interfaces in multilayer films prepared by the Physical vapour deposition (PVD) technique ensures energy dissipation and improves the toughness and crack-propagation resistance [8]. Excellent cutting performances are obtained from multilayer coatings consisting of stacked layers of metallic and covalent hard materials. Vogli et al. have analysed the hardness and wear coefficient of PVD metal/ceramic Ti/TiAlN multilayers with different designs [9,10]. They found that a multilayer film with the thickest TiAlN layers has the highest hardness and lowest wear coefficient. The mechanical performance of coatings based on TiAlN and either metallic Ti or Al interlayers has been studied [11]. The hardness and Young's modulus measured for multilayer films with Ti interlayers are of the same order of magnitude as those of TiAlN thin films, while these values are lower with Al interlayers. In some metallic nitride multilayer systems, transmission electron microscopy (TEM) and electron energy-loss spectroscopy (EELS) have evidenced intermixing, despite a coherent growth of the superlattices [12,13]. Core level spectroscopies like extended X-ray absorption fine structure have proved useful to probe intermixing within low- or large-period multilayer films [14–16], but the EELS technique has the advantage of combining imaging and investigation of the local order at the nano-scale [17].

The present work focuses on the properties of alternating $Ti_{0.54}Al_{0.46}$ and $Ti_{0.54}Al_{0.46}N$ layers deposited by reactive magnetron sputtering. An Al content of 46 at.% was chosen because it corresponds to the composition of the ternary coating exhibiting the best mechanical performances [7,18]. A set of multilayer coatings with five different periods was elaborated using a reactive gas pulsing process (RGPP) [19]. This approach should allow the fabrication of TiAl-based alloy/nitride multilayer films by radio frequency (RF) reactive magnetron sputtering with a controlled pulsing flow rate of nitrogen reactive gas. The argon flow rate was kept constant during sputtering of a sintered TiAl alloy target while the nitrogen flow rate was periodically pulsed as a rectangular wave function during deposition. This RGPP approach has already been successfully used to deposit, from one metallic target (M) and one reactive gas, O_2, single systems like metal oxynitride films (TiON [20,21], FeON [22–24], TaON, NbON [25], ZrON [26], or SiON [27]) or metal/oxide multilayer films (Ti/TiO_2, W/WO_3, Ta/Ta_2O_5 [28–30]) by pulsing oxygen gas flow. One work has been devoted to the deposition of complex systems using the RGPP process with two targets (M1 and M2) and one reactive gas N_2 by pulsing nitrogen gas flow [31]. The deposition of nitride multilayers or alloy/nitride multilayer films with a single alloy target (M1M2) and one reactive gas, N_2, has never been achieved using pulsed nitrogen flow until now. The main purpose of this work is to establish that this RGPP process using a single alloy target (TiAl) and one reactive gas, N_2, allows deposition of $Ti_{0.54}Al_{0.46}/Ti_{0.54}Al_{0.46}N$ multilayer coatings with different periods Λ and to characterize the structure and mechanical properties of as-deposited films. X-ray diffraction (XRD) and nano-indentation and friction tests were carried out on the set of films in order to investigate the influence of the multilayer period. Then, special attention was paid to the film with a period of 10 nm, which exhibits good mechanical properties. The influence of the film thickness on the hardness and indentation modulus was investigated and EELS was used to probe the local environment of nitrogen atoms within each of the two layers and thus to evaluate the degree of interdiffusion.

2. Experimental

2.1. Elaboration and multilayer design

Thin films were deposited onto silicon (100) wafer by RF magnetron sputtering in an Alliance Concept AC450 vacuum reactor. One sintered titanium/aluminium 66/33 at.% alloy target (purity 99.99%, 50 mm diameter, and 6 mm thickness) was RF sputtered at 13.56 MHz in an Ar or Ar + N_2 atmosphere. The distance between the target and the substrate was fixed at 60 mm and the temperature was kept at room temperature. The substrates and the TiAl target were cleaned before deposition. The substrates were etched in situ using argon ion bombardment in pure argon at 0.8 Pa with an applied RF bias voltage of 400 V during 15 min. The TiAl target was pre-sputtered in a pure argon atmosphere at 0.8 Pa for 15 min. The sputtering power applied was 80 W. All deposition was carried out with a constant argon flow rate of 3 sccm and a constant pumping speed of 10 $L \cdot s^{-1}$. The nitrogen flow rate was pulsed with a variable period T ranging from 44 to 480 s. During this period, the nitrogen flow rate was modulated as a rectangular wave function versus time (Table 1). The minimum and maximum nitrogen flow rates, Q_{min} and Q_{max}, were kept constant at $Q_{min} = 0$ sccm and $Q_{max} = 5$ sccm. Those conditions were chosen in order to alternate the reactive sputtering process between the alloy and compound sputtering mode, which corresponds to changing the total pressure between 0.52 Pa (alloy deposition) and 0.65 Pa (nitride deposition). The nitrogen injection time t_{on} and the nitrogen closing time t_{off} ($T = t_{on} + t_{off}$) were systematically changed for each multilayer film and calculated from the deposition rate of a single layer of alloy and nitride (Table 1). The expected period Λ for each multilayer film is defined as $\Lambda = \lambda_{TiAl} + \lambda_{TiAlN}$, with $\lambda_{TiAl} = \lambda_{TiAlN}$, where λ_{TiAl} and λ_{TiAlN} are the thicknesses of the alloy and nitride sub-layers, respectively. The deposition time was adjusted to obtain a total thickness of the film close to 2 μm (Table 1). For all samples, the first layer on the Si substrate is $Ti_{0.54}Al_{0.46}$ and the upper layer is $Ti_{0.54}Al_{0.46}N$. For Λ = 10 nm, films with different thicknesses ranging from 700 to 3200 nm were elaborated. $Ti_{0.54}Al_{0.46}$ and $Ti_{0.54}Al_{0.46}N$ single layers were also deposited to compare their properties with those of the $Ti_{0.54}Al_{0.46}/Ti_{0.54}Al_{0.46}N$ multilayer films with different periods. The element compositions were determined by energy-dispersive X-ray emission spectroscopy and wavelength-dispersive emission spectroscopy in a scanning electron microscope (SEM) under voltages of 5 and 10 kV after calibration.

2.2. Analysis methods

The crystalline structure of the films was investigated by XRD using a Rigaku Smartlab (9 kW) diffractometer equipped with a CuKα1 source (λ = 1.54056 Å) and a Ge (220) two-bounce front monochromator. XRD patterns were recorded at room temperature in θ–2θ parallel mode in the range of 35–50°. The high-angle XRD resulting from diffraction of atomic planes in the superlattice is due to convolution of the crystalline structure of the layers with the modulation of the composition [32].

TEM measurements were performed on a Cs-corrected JEOL 2100F microscope, operating at 200 kV and equipped with an EELS Gatan Imaging Filter (GIF) spectrometer. The morphology and crystalline structure were studied by high-resolution selected-area electron diffraction (SAED). Scanning transmission electron microscopy (STEM) imaging with a 0.15 nm probe was used for chemical determination of interfaces, and the GIF spectrometer fit with a collection angle set to 30 mrad and a dispersion of 0.2 eV energy channel was used to record electron energy-loss near-edge structure (ELNES) spectra. Different line scans on several interfaces were recorded on the cross-section, prepared by focused ion beam.

Table 1
Pulsed nitrogen parameters and characteristics of the multilayer films.

Pulsing period T (s)	t_{on} (s)	t_{off} (s)	$\lambda_{TiAl} = \lambda_{TiAlN}$ (nm)	Period Λ (nm)	Film thickness ef (nm)	Stacking number (ef/Λ)
480	378	102	25	50	2000	40
230	181	49	12	24	1800	75
160	123	37	8	16	1970	123
90	65	25	5	10	1790	179
44	30	14	2	4	1850	462

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