Surface & Coatings Technology 275 (2015) 120–126

Contents lists available at ScienceDirect

Surface & Coatings Technology

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

Oxidation and diffusion processes during annealing of TiSi(V)N films

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ARTICLE INFO

Article history:
Received 22 December 2014
Revised 18 May 2015
Accepted in revised form 19 May 2015
Available online 22 May 2015

Keywords:
TiSiVN system
Structural evolution
Oxidation
Oxide scale
Diffusion processes

ABSTRACT

The degradation of self-lubricant hard coatings applied in tools for high-speed cutting or dry drilling operations occurs by a combination of wear, oxidation and diffusion. The aim of this investigation was to study the effect of V additions on the diffusion processes and on the oxide scale formation during annealing of TiSiVN coatings. Relation of these results with those achieved for a reference $Ti_{0.80}Si_{0.15}N$ coating with similar Si content is also presented. The structure evolution of the $Ti_{0.65}Si_{0.11}V_{0.15}N$ film was assessed by an in-situ hot-XRD device. A dual layer oxide was formed in the case of $Ti_{0.80}Si_{0.15}N$ coating with a protective Si–O layer at an oxide/coating interface; however, in zones of film defects a complex oxide structure was developed. V additions increased the oxidation rate of the coatings as a result of the V ions diffusion throughout the oxide scale, which inhibited the formation of a continuous protective silicon oxide layer.

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1. Introduction

The reduction of the wear and friction coefficient of machining tools during in-service conditions remains an important challenge today in order to increase their life-time and performance. Traditionally, oils and other liquid lubricants have been used to reduce the friction between the cutting tool and piece primarily by shearing the oil molecules across the solid–liquid–solid interface. However, most of the liquid lubricants volatilize at high temperature, which leads to the dry sliding and consequent failure of the cutting tools resulting in the increasing machine down times, higher process instability, poor product quality and higher costs [1]. To face these problems, a wide range of solid lubricant coatings, such as WC/C, MoS_2, diamond-like carbon (DLC), h-BN as well as their combinations in nanocrystalline or multilayer structures, have been developed in the last decades and successfully applied in order to improve the tribological behavior under dry machining conditions [2–5]. However, considerable degradation of the tribological effectiveness of these coatings at elevated temperature has been reported due to their low resistance to oxidation. To overcome this shortcoming, a new concept of high temperature lubrication has been proposed. Solid lubricant coatings have been developed by combining the intrinsic properties of some binary or ternary films (TiN, CrN, CrAlN, TiAlN, YSZ, etc.), which are very hard and resistant to oxidation, with specific elements (metals), which diffuse to the surface and form a low friction tribolayer (as a metal layer, e.g. Ag, Cu, Au, Pb and In, or a low-friction oxide, e.g. V_2O_5, $Ag_2Mo_2O_7$) [6–9]. Among these elements, particular attention has been given to the vanadium-containing coatings (Magnéli phases V_nO_{2n-1}), which showed interesting tribological properties in the temperature range 500–700 °C [2,10–15]. Dissimilar series of V-based hard coatings have been developed, such as ternary CrVN [16], (V,Ti)N [17], multilayer AlN/VN [18] and quaternary single layered or multilayered AlCrVN [19,20] and TiAlVN [12,21–23]. Independent of the configuration, the friction was decreased and the wear resistance improved; however, the oxidation resistance was degraded. For example, for ternary AlCrN and TiAlN coatings the onset point of oxidation decreased to 600 °C with V incorporation [12,24,25]. In the case of the TiAlN/VN films, signals of lubricious V_2O_5 were detected as soon as the oxidation started (600 °C), while at high temperatures only $AlVO_4$ and TiO_2 were identified [12]. For AlCrVN coatings, $AlVO_4$, $(Al, Cr, V)_2O_3$ as well as V_2O_5 oxides were observed for an annealing temperature of 700 °C [25]. In these studies, the lower onset point of oxidation displayed by the V-containing coatings in relation to the host ones was explained by the reactions occurring between protective oxides and vanadium (such as formation of Al–V–O phases). Lower oxidation resistance of coatings due to V incorporation is not considered as a drawback from the tribological point of view, since the V_2O_5 oxide formed at the surface is known to reduce the friction and wear rate of coatings. Thus, as the oxidation behavior strongly affects the performance of the coatings, some studies were conducted with the aim of understanding the diffusion processes occurring during coatings annealing. Zhou et al. [24] and Franz et al. [25] studied TiAlN/VN and AlCrVN films, respectively. Zhou et al. [24] reported that a duplex oxide structure was formed during annealing of TiAlN/VN coatings for temperatures higher than 600 °C: an inner layer

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http://dx.doi.org/10.1016/j.surfcoat.2015.05.031
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comprised a porous region of Ti rich and V rich nanocrystallites, while several phases were observed in the outer region, including V_2O_5, TiO_2 and $AlVO_4$. V_2O_5 phase was dominant in the outer surface at temperatures higher than 638 °C. The outward diffusion of V depended on the species presented: in the inner layer, V was presented as V^{3+} and V^{4+}, while V^{5+} was dominant in the outer layer. The porous inner layer was attributed to V ions diffusion to the surface to form V_2O_5. Franz et al. [25] also observed the formation of two different oxide layers during annealing of AlCrVN coatings. While vanadium diffusion led to a V-depleted inner oxide (mixed or nanocrystalline $(Al,Cr,V)_2O_3$), the outer oxide mainly contained V_2O_5 and small amounts of $AlVO_4$. Despite of these investigations, very little knowledge is still available for the static oxidation of V rich coatings.

Recently we have reported the effect of V incorporation on the structure, mechanical properties, oxidation resistance and tribological behavior (at room temperature) of TiSiN films, deposited by DC reactive magnetron sputtering [26,27]. TiSiN system exhibits similar level of oxidation resistance than AlCrN and TiAlN films [28,29] (the only ternary films where the effect of V additions was studied); moreover, it can be deposited with much higher hardness depending on the structure and Si content. Lubricious vanadium oxides have been successfully detected on the oxidized surface and on the worn surface of these films, which decreased the wear rate and friction coefficient of coatings. However, as in the similar coating systems, a drop on the oxidation resistance of coatings was observed. In our specific case, the reaction of V with the protective oxide (Si–O) was not detected and therefore the decrease of the oxidation resistance could not be attributed to such reactions. Present work provides a comprehensive understanding of the oxidation mechanism/diffusion processes occurring during TiSiVN film annealing. The effect of vanadium was studied in comparison to the diffusion processes occurring during annealing of a $Ti_{0.80}Si_{0.15}N$ films, which were used as a reference. In addition, isothermal oxidation kinetics curves are included to provide a baseline.

2. Experimental procedure

TiSiN and TiSiVN coatings (labeled as $Ti_{0.80}Si_{0.15}N$ and $Ti_{0.65}Si_{0.11}V_{0.15}N$, respectively), with approximately the same silicon content and about 2.5 μm of total thickness, were deposited on alumina and FeCrAl alloy substrates in a d.c. reactive magnetron sputtering machine equipped with two rectangular, Ti (99.9%) and $TiSi_2$ (99.9%), magnetron cathodes working in unbalanced mode. V incorporation was achieved by inserting 8 pellets of vanadium into the erosion zone of Ti target. In both cases Ti–V (0.24 μm) and Ti–VN (0.45 μm) adhesion layers were deposited as bonding layers improving coating to substrate adhesion. The depositions were performed with a negative substrate bias of 50 V. In both depositions, the total working gas pressure was kept constant at 0.3 Pa, using approximately 30 sccm of Ar and 17 sccm of N_2, and the deposition temperature was lower than 300 °C. These coatings were already characterized in our previous works [26,27]. A summary of the deposition conditions and the main properties of the coatings are listed in Table 1. Temperature effect on the structure of the V rich coating was characterized in open air in-situ by hot-XRD device in the range of 500 °C to 750 °C, using a grazing incidence angle of 2° and Co Kα radiation (1.789010 Å). This range of temperature was selected based on the thermogravimetric oxidation curves of films performed at a constant linear-temperature ramp (RT (room temperature) to 1200 °C at 20 °C/min) shown in Ref. [26]. Between each selected temperature a step of 10 min holding time was allowed for thermal stabilization and 30 min time acquisition was used. Oxidation of films was assessed by thermogravimetric analysis (TGA) using industrial air (99.99% purity). $Ti_{0.65}Si_{0.11}V_{0.15}N$ and $Ti_{0.80}Si_{0.15}N$ films were isothermally tested at 600 °C during 30 min and 900 °C during 1 h, respectively. These temperatures represent main oxidation events observed in the previous thermal gravimetric oxidation curves performed at constant linear-temperature ramp [26]. After annealing, the cross section thin foils of oxidized films was prepared by a focused ion beam (FIB) and analyzed by transmission electron microscope (TEM) equipped with an energy-dispersive x-ray (EDS) spectroscopy system. Bright field scan transmission electron microscopy STEM/EDX maps and elemental profiles along the cross section of the oxidized coatings were acquired to characterize the distribution of the main elements in the films ($Ti_{0.80}Si_{0.15}N$ and $Ti_{0.65}Si_{0.11}V_{0.15}N$) and in the oxide scales.

3. Results and discussion

3.1. Characterization of the as-deposited and oxidized coatings

Firstly we will summarize the main characteristics and the oxidation resistance of $Ti_{0.80}Si_{0.15}N$ and $Ti_{0.65}Si_{0.11}V_{0.15}N$ coatings. The investigated coatings with chemical composition of $Ti_{0.80}Si_{0.15}N$ and $Ti_{0.65}Si_{0.11}V_{0.14}N$, showed a typical columnar morphology and fcc NaCl-type structure assigned to crystalline TiN with Si and V in solid solution [26]. V additions to the TiSiN coating significantly improved their mechanical and tribological properties; however, their oxidation resistance was lowered. The improvement of the tribological properties was related to V–O formation in the sliding contact, which acted as a lubricious tribo-film decreasing the friction and protecting the coating from wear [27]. Fig. 1 shows the weight gain during isothermal oxidation at three selected temperatures. Note that $Ti_{0.80}Si_{0.15}N$ film was tested at higher

Table 1
Designation, deposition conditions and main properties of the $Ti_{0.80}Si_{0.15}N$ and $Ti_{0.65}Si_{0.11}V_{0.15}N$ coatings.

Sample	TiSiN					TiSiVN				
Sample designation	$Ti_{0.80}Si_{0.15}N$					$Ti_{0.65}Si_{0.11}V_{0.15}N$				
Base pressure (Pa)	8.7×10^{-4}									
Working pressure (Pa)	0.3 Pa									
Target power density (W/cm^2)	Ti			$TiSi_2$		Ti			$TiSi_2$	
	6			1.5		6			1.5	
Substrate temperature (°C)	<300 °C									
Ar and N2 gas flow (sccm)	35 and 17									
Coatings thickness (nm)	2.5 μm									
Chemical composition	Ti	Si	V	O	N	Ti	Si	V	O	N
	41.3 ± 0.3	6.68 ± 0.03	–	0.55 ± 0.06	51.5 ± 0.2	33.6 ± 0.3	5.64 ± 0.05	7.6 ± 0.2	1.42 ± 0.13	51.71 ± 0.14
Lattice parameter (nm)	0.422					0.421				
Grain size (nm)	24					20				
Hardness (Gpa)	27 ± 2					28 ± 2				
Young's Modulus (GPa)	307 ± 10					328 ± 7				
Residual stresses (GPa)	3.4					4.1				
Onset point of oxidation	900 °C					500 °C				
Friction coefficient (room temperature) against Al_2O_3	1.07					0.51				

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