Oxidation resistance of CrN/(Cr,V)N hard coatings deposited by DC magnetron sputtering

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ABSTRACT

In recent years vanadium-doped hard coatings have become available as possible candidates for self-lubrication at high temperatures. Their low coefficient of friction has mainly been attributed to the formation of the V_2O_5 phase. However, the formation of vanadium oxides must be controlled by the out-diffusion of vanadium in order to achieve the combination of a low coefficient of friction and good mechanical properties for the protective coatings. In this work the application of a nanolayer of CrN/(Cr,V)N hard coating was proposed as a way to better control the out-diffusion of vanadium, while the topmost chromium oxide layer acts as barrier for the vanadium diffusion. However, the aim of this investigation was not only to focus on the formation of the oxide layer. Special attention was given to the oxidation process that takes place at the growth defects, where we observed a strong diffusion of vanadium taking place. The CrN/(Cr,V)N nanolayer coatings were deposited by DC unbalanced magnetron sputtering in an CC800/9 (CemeCon) industrial unit. The vanadium concentration in the (Cr,V)N layers was varied in the range 1.0–11.5 at.%.

1. Introduction

The formation of high-temperature lubricious oxides on ceramic coatings has seen great interest over the past 10 years because such coatings are potential candidates for the protection of hot-forging tools. The tribological testing of VN coatings revealed the formation of such oxides at temperatures above 500 °C. The low-friction effect is attributed to liquid lubrication due to the formation of V_2O_5 with easily shearable planes (typical for Magneli phase oxides) and a low melting point (around 670 °C). The problem is that the intensive oxidation of VN at elevated temperatures has a tendency to increase the wear rates. In addition, from the application point of view it is very important that the coating also retains sufficient mechanical integrity at high temperatures. Therefore, the oxidation process must be controlled by the out-diffusion of vanadium. In order to design such coatings, the incorporation of vanadium into existing, well-established, hard coatings like TiN, CrN or TiAlN has been tested [1–5]. At elevated temperatures the out-diffusion of the vanadium ions through the oxide scale formed on the surface of such coatings is far slower, but still fast enough to ensure a low coefficient of friction. The formation of lubricious oxides can be controlled by the vanadium's out-diffusion, while the matrix of

the unoxidized coating retains the required mechanical properties. Such vanadium-based coatings offer a combination of a low coefficient of friction and a low rate of wear. The addition of vanadium also increases the hardness due to the solid-solution hardening effect.

Various vanadium-containing coatings have been studied, such as CrVN [1], TiVN [2], multilayer AlN/VN [3] and a quaternary single and multilayer based on CrAlVN [4,5] and TiAlVN [6–9]. The findings suggested that the addition of vanadium decreased the coefficient of friction for all these binary and ternary systems at temperatures in the range 550–700 °C.

Different approaches have been proposed in order to control the out-diffusion of vanadium. Fernandes et al. [10] studied a TiSiN nano-composite coating doped with vanadium. They analysed the effect of increasing the vanadium content on Ti–Si–V–N coatings and found that the vanadium diffusion in $a-Si_3N_4$ is much slower than in TiN. With an increasing amount of amorphous nitride phase they optimized the size of the TiN grains and were thus able to control the vanadium diffusion in the nanocomposite TiSiN films. However, larger amounts of $a-Si_3N_4$ phase also lead to a reduction in the mechanical properties.

In this study a nanolayer CrN/(Cr,V)N hard coating was investigated to see whether it could better control the vanadium out-diffusion. It is based on the idea that the top chromium oxide layer acts as a diffusion barrier to the vanadium ions during the oxidation at elevated temperatures (>500 °C) due to the immiscibility between the vanadium oxides

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Table 1
Vanadium content (V_{EDX}), thickness of as-deposited coating (t), microhardness (HV), lattice parameter a_{hkl}, surface roughness S_a, internal stress (σ), *critical force for scratching force jump* ($L_c(F_t)$), activation energy for oxidation (E_a) and parabolic oxidation constant k_0 for (Cr,V)N coatings with different compositions as well as for the binary CrN and VN coatings.

Coating	V_{EDX}	t	HV	a_{111}	a_{200}	σ	S_a	$L_c(F_t)$	E_a	k_0
	(at%)	(μm)		(nm)	(nm)	(GPa)	(nm)	(N)	(eV)	($\mu g^2/cm^4 min$)
CrN	0	3.5	1800	0.4156		0.49			2.2 ± 0.2	2.5×10^9
CrN/(Cr,V)N	0.8	9.2	1850	0.4004	0.4141		206	94		
CrN/(Cr,V)N	1.3	8.7		0.3989	0.4134		184	91		
CrN/(Cr,V)N	2.5	7.9	2250	0.3993	0.4133	0.43	180		2.5 ± 0.2	2.6×10^{14}
CrN/(Cr,V)N	4.0	7.6		0.3993	0.4132		74	79		
CrN/(Cr,V)N	5.9	6.7		0.4019	0.4131	0.89	58			
CrN/(Cr,V)N	7.6	6.6	2400	0.4047	0.4126	1.52	51	83	2.4 ± 0.2	4.2×10^{13}
CrN/(Cr,V)N	9.1	6.4		0.4066	0.4129					
CrN/(Cr,V)N	10.2	5.8	2296	0.4088	0.4133	1.95	88	84	2.4 ± 0.2	8.3×10^{13}
CrN/(Cr,V)N	11.0	4.7		0.4115	0.4135	2.8	75		2.4 ± 0.2	1.2×10^{14}
CrN/(Cr,V)N	11.5	3.6	2500	0.4160	0.4144		43	90		
VN	50	3.0	2400	0.413*					1.2 ± 0.2	4.3×10^9

* According to ICDD.

and the chromium oxides. Special attention is given to the role of the growth defects in the oxidation process [11].

2. Experimental

All the coatings were deposited by DC magnetron sputtering in a CC800/9 (CemeCon) industrial unit. The deposition system is equipped with four unbalanced magnetron sources arranged in the corners of a chamber. The nanolayer CrN/(Cr,V)N coatings were deposited from one pair of chromium and one pair of Cr/V triangular targets. In this way a set of samples with a composition gradient along the chamber's vertical axis were deposited in a single process. The vanadium concentration in the (Cr,V)N layers was varied in the range 1.0–11.5 at.%. The composition of the as-deposited (Cr,V)N coatings was measured by energy dispersive analysis of X-rays (EDX, Oxford Instruments, INCA 350 EDX system fitted with SDD detector), which is attached to a scanning electron microscope (SEM, JEOL JSM-7600F). The substrates (polished steel, alumina, cemented carbide (HM), silicon wafer) were mounted on a two-fold rotating substrate holder. By using double rotation it was possible to produce nanolayered coatings with a uniform thickness of the constituent layers. The steel samples were ground and polished using 3-μm-diamond polishing paste. All the samples were ultrasonically cleaned and sputter-etched prior to the deposition of the coating. MF ion etching with bias on a turntable of 650 V was conducted for 75 min in mixed argon (flow rate 120 ml/min) and krypton (flow rate 90 ml/min) atmosphere under a pressure of 0.35 Pa. After loading, the vacuum chamber was evacuated to a base pressure of 3 mPa. The total operating pressure was maintained at 0.6 Pa, with the flow rates of nitrogen, argon and krypton being 100, 160 and 110 ml/min, respectively. Prior to the coating, the deposition chamber was heated to 450 °C.

The adhesion of the coating was assessed using the scratch-test method with a Revetest scratch tester (loading rate 100 N/min, scratching rate 10 mm/min, loading range 0–100 N). The sample curvatures, thickness and roughness were measured using a Taylor–Hobson Talysurf 2 profilometer.

The coatings were oxidized by annealing the samples in a tube furnace at temperatures in the range 600–750 °C with an oxygen flow. Periodically, the specimens were taken out of the furnace and weighed using a precise microbalance (Mettler Toledo UM3). In addition, the oxide products were analysed by X-ray diffraction (XRD) using Bragg–
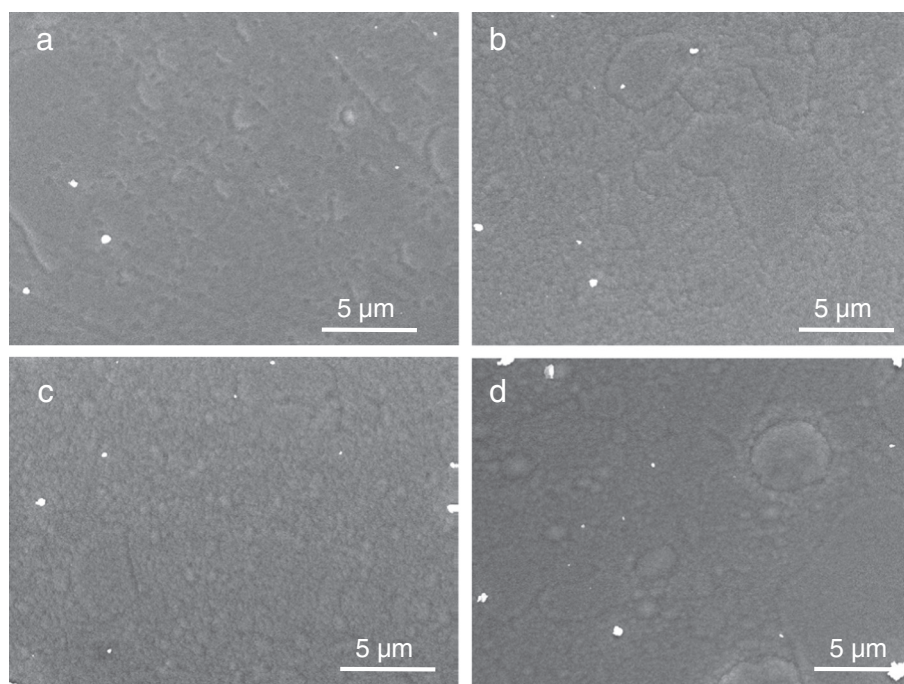

Fig. 1. Top-view SEM image of the CrN/(Cr,V)N coating with different vanadium contents deposited onto D2 tool steel substrate: 11 at.% (a), 9 at.% (b), 5.8 at.% (c) and 1.2 at.% (d).