Oxidation processes in vanadium-based single-layer and nanolayer hard coatings

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ABSTRACT

We studied the oxidation resistance of CrVN single-layer, CrN/(Cr,V)N nanolayer and CrN/(Cr,V)N/VN nanolayer hard coatings with respect to the Cr:V atomic ratio. All the coatings were deposited by DC magnetron sputtering in an industrial deposition system. Using different target configurations we were able to prepare a series of samples with various Cr:V ratios. The following target arrangements were used: a) two sources with triangle-like, segmental Cr/V targets for depositing a single-layer CrVN coating with different Cr:V atomic ratios; b) two triangle-like, segmental Cr/V targets and two chromium targets for depositing the nanolayer CrN/(Cr,V)N coating; and c) two triangle-like, segmental Cr/V targets, one chromium and one vanadium target for depositing the nanolayer CrN/(Cr,V)N/VN coating.

The analysis of the oxidation mechanisms for all three types of coatings showed that the formation of a thin chromium oxide layer slows down the diffusion of vanadium towards the surface. However, at the locations where the growth defects were present the vanadium kept diffusing at high rates and formed V_2O_5 dendritic structures at the surface. Vanadium oxide is known to have good lubricating properties at elevated temperatures, thus (Cr,V)N-based hard coatings could potentially be useful for the protection of hot-forging tools operating at high temperatures.

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1. Introduction

Hot-forging tools are exposed to extreme working conditions, such as a cyclic contact with the workpiece materials at temperatures above 1000 °C [1,2]. During the forging operation the workpiece material and hard particles (like scale and oxides) glide at high velocity relative to the tool surface under the action of high pressure, causing abrasive wear. On the other hand, high temperatures, which act simultaneously with strong forces, cause a sticking of the workpiece material on the tool's surface, leading to adhesive wear. Additionally, the cooling and lubrication of the tool after each forming operation lead to thermal shocks. The cyclic thermal loads also affect the microstructure of the tool, which then leads to a reduction in the hardness and plastic deformation of the tool material. All these mechanical, tribological, chemical and thermo-cyclic loads interact with each other and eventually cause failure of the forging tools. Depending on the specific operation, one of these processes dominates and is the ultimate cause of the tool's failure.

Today, effective protection against wear for hot-forging tools remains a major challenge. To increase the lifetime of such tools it is mainly duplex treatments that are used [1]. Typically, the hot-working tool steel is first pre-treated with plasma nitriding and then coated with a hard and lubricious coating. In order to reduce both the wear rate and the friction coefficient at high temperatures, three properties of the hard protective coating are important. First, it should reduce the diffusion rate and thus lower the chemically and thermally induced tool wear. Second, it should have a high hot hardness, resulting in a lower abrasion rate. Third, it should have a low friction coefficient at high temperatures.

Most promising coatings that fulfil these requirements are vanadium-based, self-lubricating, PVD hard coatings. Such coatings form solid vanadium oxides with a very low friction coefficient at temperatures >500 °C [3]. Vanadium oxide is known to have good lubricating properties at elevated temperatures due to its low melting point (670 °C). The low-friction effect is also attributed to weakly bonded and easily shearable lattice planes in the crystal structure (typical for Magneli phase oxides). The diffusion of vanadium to the top of the coating is a necessary condition, which provides continuous, self-lubricating effect during the operation of the coated tools. However, the out-diffusion of vanadium should

not be too fast, while a too intensive diffusion of vanadium deteriorates the mechanical integrity of the coating. From this point of view, a simple VN hard coating is not appropriate because of rapid oxidation at elevated temperature.

In the literature, different approaches have been reported in order to reduce the diffusion of vanadium towards the surface. Series of V-based hard coatings have been developed by incorporating vanadium as a solid solution into existing hard coatings like CrN [4], TiN [5], TiAlN [6,7], AlCrN [4,8,9], TiSiN [10] and CrAlSiN [11]. Another possibility, which is explored in the literature, is the deposition of different VN-based multilayer coatings such as AlN/VN [12], CrN/VN [13], TiAlN/VN [14], TiAlCN/VCN [15], CrAlN/VN [16] and CrAlSiN/TiVN [17]. Both approaches make possible a combination of high wear resistance and the formation of lubricious oxides at high working temperatures.

In our previous work [18] we evaluated the design of a nanolayer hard coating composed of CrN and (Cr,V)N layers. We found that in such a structure the bulk diffusion of vanadium is reduced by the formation of a topmost Cr-oxide layer, while the diffusion of vanadium was localized on growth defects. From the application point of view such behaviour is important because it localizes the diffusion of vanadium and thus reduces the overall diffusion towards the surface. A knowledge of the oxidation kinetics of vanadium-based coatings is thus essential for understanding the fundamental processes and also for the practical application of such coatings. Due to the specific target configuration during the deposition we were not able to prepare the nl-CrN/(Cr,V)N nanolayer coating with a vanadium content of more than 12 at%.

The objective of this work was to design nanolayer coating systems composed of CrN, (Cr,V)N and VN layers. For deposition of such coating we used the similar target configuration as for nl-CrN/(Cr,V)N coating except one chromium target was replaced with vanadium. In such a way we increased the maximum vanadium content up to 25 at%. We studied the oxidation resistance of such coatings in comparison with a (Cr,V)N single-layer coating and previously designed CrN/(Cr,V)N nanolayer coatings. The composition of the (Cr,V)N hard coatings was changed for wide compositional variations by employing triangle-like, chromium and vanadium targets.

2. Experimental

All the coatings were deposited using a CC800/9 (CemeCon) industrial DC-magnetron sputtering system. The deposition system is equipped with four unbalanced magnetron sources arranged in the corners of a chamber. The following types of coating were deposited (Fig. 1):

a) a single-layer CrVN coating with different Cr:V atomic ratios was prepared using only two sources with triangle-like, segmental Cr/V targets positioned on one side of the vacuum chamber (Fig. 1a)
b) a nanolayer CrN/(Cr,V)N coating was deposited using two triangle-like, segmental Cr/V targets (positioned on opposite sides of the vacuum chamber) and two chromium targets (Fig. 1b)
c) a nanolayer CrN/(Cr,V)N/VN coating was prepared using two triangle-like, segmental Cr/V targets (positioned on opposite sides of the vacuum chamber), one chromium and one vanadium target (Fig. 1c).

Using triangle-like, segmental Cr/V targets a set of coatings with a composition gradient along the chamber's vertical axis was deposited in a single process (Fig. 1d). The compositions of the as-deposited (Cr,V)N coatings were measured from the energy-dispersive analysis of X-rays (EDX, Oxford Instruments, INCA 350 EDX system fitted with an SDD detector) attached to a scanning electron microscope (SEM, JEOL JSM-7600F). The substrates, which included polished tool steel, cemented carbide (HM), silicon wafer, polished alumina (coated with thin Cr layer in order to assure the electrical contact during deposition processes), 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. After loading, the vacuum chamber was evacuated to a base pressure of 3 mPa. Ion etching with an mid-frequency (MF) bias on a turntable (650 V) was conducted for 75 min in a mixed argon (flow rate 120 ml/min) and krypton (flow rate 90 ml/min) atmosphere under a pressure of 0.35 Pa. 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 depth profiles were measured by Auger spectrometry in a PHI SAM 545 spectrometer in order to gain information about the diffusion processes. For the electron excitation a primary electron beam of 3 keV and 1 μA, with a diameter of 40 μm, was used. During depth profiling the samples were sputtered by two symmetrically inclined argon ion beams of 1 keV at an ion incidence angle of 47° with respect to the surface normal. The oxide products were analysed by X-ray diffraction (XRD) using the Bragg—Brentano geometry. The XRD measurements were conducted on a Bruker AXS Endeavor D4 diffractometer with Cu-Kα1 radiation (0.15406 nm).

Annealing of the samples was carried out in an oxygen atmosphere at 600—750 °C. The time of annealing was in the range of 0.5—20 h, depending on the vanadium content and coating design.
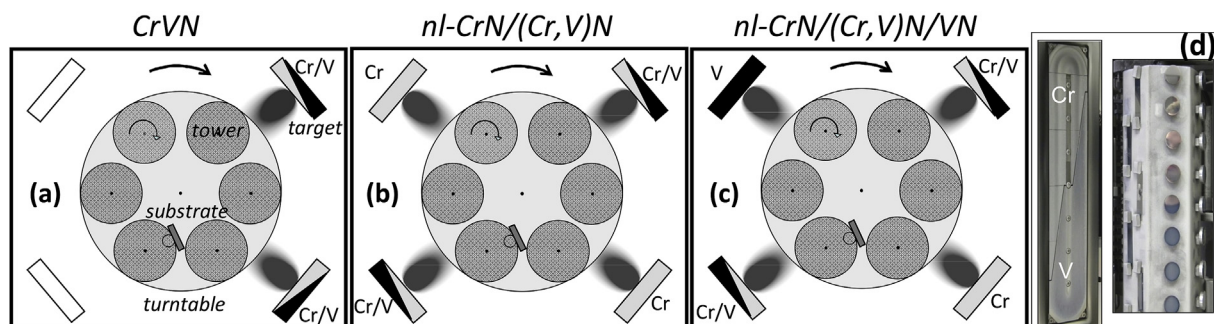

Fig. 1. Configurations of the targets for the deposition of the (Cr,V)N single-layer (a), CrN/(Cr,V)N nanolayer (b) and CrN/(Cr,V)N/VN nanolayer (c) coatings. Photograph of the triangle-like segmental Cr/V target and the substrate holder with a series of samples positioned on the vertical shaft (d).