Oxidation of vanadium nitride and titanium nitride coatings

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Abstract

The oxidation of vanadium nitride (VN) and titanium nitride (TiN) coatings in ultra-high vacuum has been investigated in situ by X-ray photoelectron spectroscopy. On the VN coatings mixed oxide layers containing V^{3+} and V^{4+} species form at elevated temperatures (≥600°C) and at high oxygen exposures, which cover completely the VN surface. Under similar oxidation conditions the TiN surface oxidises partially to a mixture of TiO_2 and Ti oxynitride (TiO_xN_y) phases. This oxidation behaviour has been correlated to the tribological properties of the VN and TiN coatings investigated recently.

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1. Introduction

Transition metal nitrides have long been of interest due to their excellent physical and chemical properties, such as high melting point, metallic conductivity, good chemical stability, and high mechanical hardness [1,2]. Owing to these properties transition metal nitrides have a wide-range of technological applications, e.g. as wear and corrosion resistant coatings, field emitters, superconductors and buffer layers in microelectronics. In particular, titanium nitride (TiN) is often used as hard coatings on machining tools, due to its chemical inertness against many workpiece materials, while vanadium nitride (VN) has been recently suggested because of its low friction coefficient at elevated temperatures. It has been proposed [3] that the latter is caused by the formation of surface oxide phases that contain easy shearable crystallographic defect planes, the so-called Magnéli type oxides, which may act as self-lubricants.

Recently, the tribological properties of VN and TiN coatings have been investigated and correlated to the oxide phases formed during high temperature treatments under atmospheric pressure [4]. In order to gain more insight into the oxidation mechanism of VN and TiN coatings at different temperatures we have investigated in this work the oxidation behaviour of these materials under ultra-high vacuum (UHV) conditions by X-ray photoelectron spectroscopy (XPS). This experimental approach offers several advantages, in particular when dealing with ultrathin oxide layers, which are of relevance for the tribological properties. First, it allows a controlled oxygen exposure of the investigated samples in an atmosphere free of residual gas impurities. Second, this treatment is followed by a subsequent characterisation in situ by XPS, a technique which is both surface sensitive and element specific. In addition, it allows to identify the oxidation state of the evolving oxide phases via the characteristic chemical shifts of the transition metal core electron energy levels.

We have found in this study that on VN coatings at high oxygen exposures (≥5 × 10^4 L) and at elevated temperatures (≥600 °C), several atomic layers thick and homogeneous V-oxide layer forms and cover the surface which consists of Magnéli-type mixed-valence oxides with oxidation states between 3^+ and 4^+. Under similar oxidation conditions the TiN surface becomes only partially oxidised to a mixture of TiO_2 and TiN_xO_y phases.
2. Experimental

The VN and TiN coatings were deposited from V and Ti targets, respectively, with an unbalanced DC magnetron sputtering system and a reactive Ar + N₂ discharge, described in more detail in Ref. [4]. The XPS experiments have been performed in a commercial Perkin–Elmer ESCA 5000C UHV system operating at a base pressure of $1 \times 10^{-10}$ mbar, employing a hemispherical analyser and a standard Al Kα excitation source ($h\nu = 1486.6$ eV). The pass energy of the analyser was set at 44.8 eV and 17.9 eV for survey and high-resolution scans, respectively. All XPS spectra have been collected at an emission angle of 40° with respect to the surface normal. The binding energy (BE) scale has been calibrated by measuring the Au 4f₅/₂ peak (BE = 84.0 eV) of a reference Au sample. The XPS spectra in the V 2p–O 1s and Ti 2p core-level regions have been analysed by a peak-fitting procedure, using a Shirley-type of background and mixed Gaussian/Lorentzian peak shapes. The ex situ prepared VN and TiN samples have been transferred into the UHV system via a fast entry load-lock and subjected to Ar⁺ ion sputtering (ion beam energy of 3 keV) at room temperature to remove the contaminated surface layer. Oxygen has been dosed in the UHV system via a leak valve and the oxygen exposure is given in Langmuir (L), $1 \text{ L} = 1 \times 10^{-6}$ Torr. The oxygen pressure has been varied between $1 \times 10^{-7}$ mbar, for exposures $<50 \text{ L}$, and $1 \times 10^{-5}$ mbar for exposures $>10^4 \text{ L}$. Prior to the oxygen treatments, the atomic composition of the VN and TiN coatings has been determined by XPS phase analysis. The TiN sample shows a fully stoichiometric composition, whereas the VN stoichiometry was VN₀.₈, which is possibly influenced by preferential sputtering of N in VN during the Ar⁺ bombardment cleaning cycle.

3. Results and discussion

3.1. Oxidation of vanadium nitride coatings

Fig. 1 demonstrates the evolution of XPS spectra taken in the V 2p–O 1s (a) and N 1s (b) core-level regions as a function of the oxygen exposure of VN coatings at 25 °C.
(room temperature), 250 and 600 °C. Selected spectra of Fig. 1a have been least-squares fitted by various core-level components and the results are reported in Fig. 2. The bottom spectra of Figs. 1a and 2 (labelled VN) correspond to the pristine VN surface, which has been obtained after extended Ar⁺ sputtering at room temperature. The V 2p doublet shows a pronounced asymmetry at the higher binding energy side and requires at least two contributions in the peak deconvolution analysis. The major component (labelled 1 in Fig. 2) has a binding energy BE of 513.5 eV, which is compatible with the BE values cited in the literature for bulk vanadium nitride [5,6]. The other two minor components (labelled S) have higher binding energies of 515.1 eV and 516.8 eV, which formally correspond to an emission from oxidized V atoms with an oxidation state of >3⁺, but the overall spectral weight of these components does not scale with the low intensity of the corresponding O 1s peak. We interpret these peaks as shake-up satellites which originate from poorly screened core-hole states in VN. Such satellite structures are well documented for VN and TiN films, and their intensity was observed to vary significantly with the film stoichiometry [6–8]. Exposing the VN surface to molecular oxygen at room temperature (25 °C) causes an increase of asymmetric broadening of the V 2p peaks at the higher BE side, which is accompanied by a slow increase of the O 1s peak intensity (Fig. 1a, left panel). The V 2p spectrum taken after an O₂ dose of 10⁴ L at 25 °C (see Fig. 2 for more details) is now dominated by two core level components: the component 1 is as before due to the bulk VN phase, whereas the component 2 (yellow shaded) has a BE of 515.3 eV which is compatible with a V₂O₃ phase.¹ Since the low BE VN satellite structure (BE = 515.1 eV) overlaps with the V-oxide component, only the higher BE satellite peak has been considered in the fitting analysis. Dosing the same amount of oxygen (10³ L) at 250 °C does not lead to significant changes, only a slight increase of the intensities of the V 2p components 2 and the O 1s peak is visible, indicating a further slow growth of the V₂O₃ phase on the VN surface at 250 °C.

More drastic changes occur upon VN oxidation at 600 °C. For oxygen exposures exceeding 10⁴ L, the substrate component 1 vanishes completely and only two broad V-oxide components are present in the V 2p line shape (top spectrum in Fig. 2). The component 2 has a BE of 515.2 eV and can be ascribed again to V³⁺ species. The component 3 with a BE of 516.6 eV dominates the V 2p spectrum and originates from higher oxidized V-oxide compounds with an oxidation state higher than 3⁺. Since single valence oxides, such as VO₂ and V₂O₅, typically show much narrower V 2p lines, we tend to assign the component 3 to a mixed-valence oxide, containing V⁴⁺ and defective oxide phase, such as e.g. V₂O₅, V₃O₇, or V₆O₁₁, where broad V 2p line shapes have been observed [9]. The latter oxides obey the general formula VₓO₂ₓ₋₁, which is characteristic for the Magnéli phases. This assignment is also supported by the O 1s/V 2p peak ratio (corrected for the respective sensitivity factors [10]) of 1.85, which confirms the presence of different oxide phases with varying oxidation states of V ranging between 3⁺ and 4⁺. The formation of higher V-oxides (V⁵⁺) is probably limited by the kinetics in the UHV type experiment. Indeed, for VN coatings heated at 600 °C, but under atmospheric pressure conditions, VO₂ and V₂O₃ phases have been detected in X-ray diffraction and Raman spectra [4].

The N 1s core level spectra (Fig. 1b) reveal further details on the oxidation process of vanadium nitrides at different temperatures. Fig. 3a demonstrates the evolution of the N 1s integrated intensity with the oxygen dose. The N 1s spectrum of the clean VN surface shows a peak at 397.6 eV which is typical for VN compounds [5,6]. Oxygen exposure at 25 °C and 250 °C causes almost no change in the N 1s peak position, the N 1s intensity decreases by only 10% after the maximum dose of 10⁴ L. This suggests that the V₂O₃ phase, which forms at the VN surface under these preparation conditions, is either very thin or heterogeneously dispersed over the surface, leaving the substrate N 1s signal almost unaffected. However, at 600 °C and higher oxygen exposures (≥1×10⁴ L) the substrate N 1s signal becomes more strongly attenuated and after a dose of 5×10⁴ L it vanishes completely. This is significant and indicates that the V-oxide layer formed at 600 °C homogeneously covers the entire VN surface and has a thickness exceeding the effective attenuation length of the N 1s

¹ For interpretation of color in Fig. 2, the reader is referred to the web version of this article.
photoelectrons, which for the kinetic energy of ~1100 eV is of the order of 30 Å [11].

Fig. 3b compares the evolution of the integrated O 1s peak areas with the oxygen dose for different temperatures. At 25 °C and 250 °C the oxygen uptake shows a slow logarithmic increase with the oxygen dose (note the log scale of the X-axis). The oxidation of the VN coatings in this temperature range thus follows the so-called “low-temperature oxidation” mechanism of the Cabrera–Mott nomenclature [12], typical for thin (several atomic layers) oxide growth, where the driving force is the electric field established by the oxygen anions and their image charge. At 600 °C the oxidation rate deviates significantly from the logarithmic dependence, suggesting an oxidation mechanism different to those at 25 °C and 250 °C.

3.2. Oxidation of titanium nitride coatings

Fig. 4 shows a set of XPS spectra taken in the Ti 2p (a), N 1s (b) and O 1s (c) core-level regions as a function of the oxygen exposure of TiN coatings at 25, 250 and 600 °C. Selected spectra of Fig. 4a have been least-squares fitted by various core-level components and the results are presented in Fig. 5. The clean TiN Ti 2p3/2 spectrum is described by a major peak at 455.1 eV (labelled 1) and by a shake-up satellite at 457.9 (labelled S), specific to TiN [8]. Dosing 10 L oxygen at 25 °C leads to an increase of the intensity at the position of the S peak, which is due to the oxidation of Ti atoms. Further oxygen dosing up to 10⁴ L, however, causes no change (see also corresponding O 1s spectra in Fig. 4c), which indicates that a passivating oxide layer forms on the TiN surface. The decomposition analysis of the Ti 2p spectrum after 10³ L O₂ at room temperature (Fig. 5) shows that this oxide layer is characterized by a broad component (labelled 2) with a BE very close to that of the shake-up peak (457.9 eV), which is between the binding energies of bulk-type Ti₂O₃ (456.5 eV) and TiO₂ (458.5 eV) compounds. It has been argued previously that ultrathin oxides, or so-called oxide nanolayers on metal supports, typically exhibit XPS peaks with binding energies different to their bulk counterparts, due to the interface bonding or to the improved core-hole screening from the conductive substrate [13,14]. We thus tend to assign peak 2 to a typical surface Ti-oxide layer whose stoichiometry is specific to the interface. The oxidation of TiN at 250 °C seems to proceed initially in a similar manner. Also here, after the initial increase of intensity of the Ti 2p component 2 and of the O 1s peak, no further changes are observed up to an O₂ dose of 10³ L. However, at higher oxygen exposures both signals continue to grow faster. The peak decomposition analysis of the Ti 2p spectrum taken after 5 × 10⁴ L oxygen (see Fig. 5) shows that two new core-level components (labelled 3 and 4) evolve from peak 2, with binding energies of 458.6 eV and 457.2 eV, respectively. The former is compatible with a TiO₂ stoichiometry [15], and it dominates the Ti 2p spectrum obtained after the maximal oxygen dose of 5 × 10⁴ L at 600 °C (top curve in Fig. 5), indicating that the TiN surface is partially oxidised to TiO₂. However, in comparison to VN, the bulk TiN component 1 is still present in the Ti 2p line shape and also the N 1s signal is not completely suppressed, which demonstrates that the TiO₂ layer on the TiN sample is by far not as complete as the V-oxide layer on the VN sample. To understand the nature of component 4 in the Ti 2p spectra, it is instructive to examine the N 1s spectra (Fig. 4b). At room temperature the N 1s spectra exhibit no change in both position and intensity with the oxygen dose, showing a peak at 397.4 eV which is characteristic for TiN [8]. The same holds for the oxidation sequence at 250 °C, where only after large O₂ doses (>10⁴ L) some reduction of the intensity is observed and a shoulder at the lower BE side appears (indicated by an arrow in Fig. 4b). At 600 °C and after large oxygen exposures this shoulders develops into a single peak at 396.6 eV. N 1s core-level shifts to lower BE’s of up to 1 eV have been reported in the literature for Ti oxynitride (TiNₓOᵧ) compounds [16,17]. The corresponding Ti 2p binding energy is close to that of Ti₂O₃ compounds. We therefore attribute the component 4 with the BE of 457.2 eV to the formation of a TiNₓOᵧ phase, which evolves simultaneously with the TiO₂ growth at oxygen exposures above 10³ L and temperatures exceeding 250 °C.
Fig. 6 summarises the evolution of the integrated intensities of the N 1s (a) and O 1s (b) core-level peaks with the oxygen dose at different temperatures. The N 1s signal (Fig. 6a) decreases slowly at 25°C and 250°C with the O2 exposure, whereas at 600°C and above 10^3 L a much faster decrease is observed. However, in contrast to VN, the N 1s intensity is not completely attenuated after the maximal oxygen dose on TiN coatings. This is due partly to the smaller thickness of the TiO2 layer, but also to the presence of the TiOxNy phase, as discussed above. The O 1s intensity (Fig. 6b) shows after the initial increase a plateau with a width and height which is temperature dependent: the lower the oxidation temperature, the wider the plateau and the lower its height. We associate this plateau region with the formation of the passivating TiOx layer on the TiN surface, whose thickness increases with the temperature. Above 10^3 L oxygen and temperatures \( \geq 250 \) °C the O 1s signal increases again, which is associated with the growth of TiO2 and TiOxNy phases, as discussed above.

The results obtained here can be compared with a recent study on the tribological behaviour of VN and TiN coatings [4]: it has been shown that the VN coatings exhibit a continuous decrease of the friction coefficient above 400°C, which has been attributed to the presence of highly oxidised V-oxide phases, such as VO2 and V2O5. In contrast, only minor changes of the friction coefficient with the temperature have been found on TiN coatings. This lacking self-lubrication behaviour has been related tentatively to the formation of some titanium oxide phase on the TiN surface. Theoretically, rutile (TiO2) and other titanium oxides...
should show a lubricating effect, but some chemical and structural compositions have to be fulfilled, namely, rutile has to develop planar defect structures which appear to happen only in the stoichiometric range of TiO$_{1.98}$–TiO$_{1.93}$ [18–20]. For other stoichiometries, no low friction effect has been observed. The present study is in full accordance with the tribological study [4] and allows us to draw further conclusions. The formation of defective V-oxide phases on VN surfaces under severe oxidation conditions has been confirmed. On TiN surfaces, a Ti oxynitride phase has been detected at highly oxidative conditions which may be responsible for the poor self-lubrication properties of this material since it is not a Magnéli-phase oxide.

4. Summary

In summary, we have investigated the oxidation behaviour of VN and TiN coatings in situ by XPS. At moderate temperatures (≤250 °C) and oxygen doses up to $10^4$ L both VN and TiN surfaces become covered by ultrathin (only few atomic layers) oxide films, where the metal cations exhibit a maximum oxidation state of 3+. At higher temperatures (≥600 °C) and oxygen exposures up to $10^5$ L much thicker (≈30 Å) and homogeneous V-oxide layer covers the entire VN surface, which contains mixed-valence (between 3+ and 4+) oxide phases. Under similar oxidation conditions the TiN surface becomes only partially oxidised to a mixture of TiO$_2$ and TiN$_x$O$_y$ phases.

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