Available online at www.sciencedirect.com
ScienceDirect
ELSEVIER
Surface Science 601 (2007) 1153–1159
SURFACE SCIENCE
www.elsevier.com/locate/susc

Oxidation of vanadium nitride and titanium nitride coatings

A. Glaser [a], S. Surnev [a,*], F.P. Netzer [a], N. Fateh [b], G.A. Fontalvo [b], C. Mitterer [b]

[a] *Institute of Physics, Surface and Interface Physics, Karl-Franzens University Graz, A-8010 Graz, Austria*
[b] *Department of Physical Metallurgy and Materials Testing, University of Leoben, A-8700 Leoben, Austria*

Received 27 September 2006; accepted for publication 6 December 2006

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 ($\geqslant$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.

Keywords: VN; TiN; Hard coatings; XPS; Titanium oxides; Vanadium oxides

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 ($\geqslant 5 \times 10^4$ L) and at elevated temperatures ($\geqslant$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.

---

[*] Corresponding author. Tel.: +43 316 380 8553; fax: +43 316 380 9816.
E-mail address: svetlozar.surnev@uni-graz.at (S. Surnev).

0039-6028/$ - see front matter © 2006 Elsevier B.V. All rights reserved.
doi:10.1016/j.susc.2006.12.010

2. Experimental

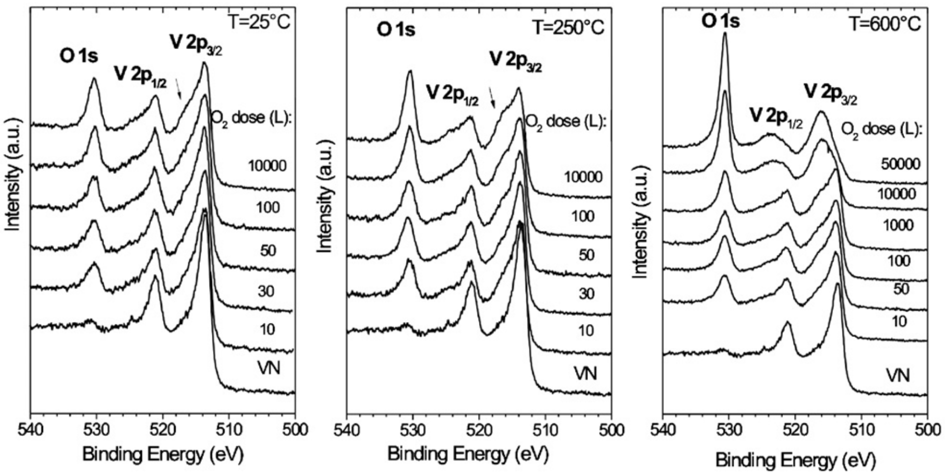
The VN and TiN coatings were deposited from V and Ti targets, respectively, with an unbalanced DC magnetron sputtering system and a reactive $Ar + N_2$ discharge, described in more detail in Ref. [4]. The XPS experiments have been performed in a commercial Perkin–Elmer ESCA 5000C UHV system operating at a base pressure of 1×10^{-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 $4f_{5/2}$ 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/Lorenzian 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), $1\ L = 1 \times 10^{-6}$ Torr. The oxygen pressure has been varied between 1×10^{-7} mbar, for exposures <50 L, and 1×10^{-5} mbar for exposures $>10^4$ 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 $VN_{0.8}$, 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

(a) V 2p - O 1s



(b) N 1s

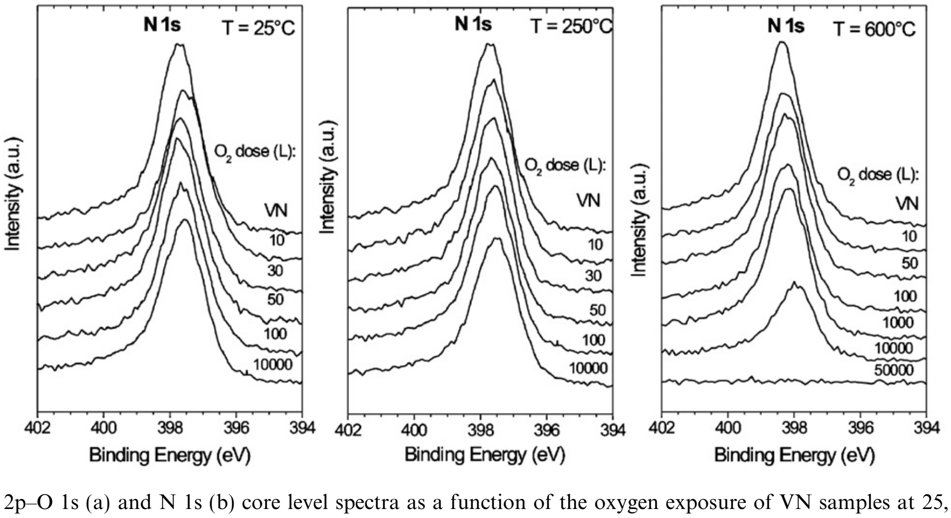


Fig. 1. Set of V 2p–O 1s (a) and N 1s (b) core level spectra as a function of the oxygen exposure of VN samples at 25, 250 and 600 °C.