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# Growth phenomena in room temperature pulsed laser deposited chromium and chromium nitride coatings

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## Abstract

Oxygen is usually found as a contaminating species in chromium (Cr) and chromium nitride (CrN<sub>x</sub>) coatings grown by various PVD techniques (e.g. sputtering, arc evaporation). The current work shows that the high energetic pulsed plasma conditions in the Pulsed Laser Deposition (PLD) technique intensify the oxygen trapping in Cr and CrN<sub>x</sub> coatings and strongly influence their microstructure. Cr-based coatings were deposited by an industrially designed 4-beam PLD evaporation system at room temperature (25 °C) by using Nd:YAG laser radiation (wavelength: 1064 nm) for Cr target ablation in N<sub>2</sub>/Ar gas mixtures. Due to the decrease of the oxygen content in films of higher thickness the source of O<sub>2</sub> was found to be the rest gas atmosphere after evacuation to pressures lower than  $2 \times 10^{-3}$  Pa. Coatings deposited from the pure metallic Cr targets in Ar rich atmospheres possess a very fine-grained  $\alpha$ -Cr phase structure with strongly increased lattice parameters resulting from the exchange of Cr by O atoms on bcc lattice sites. In contrast, high N<sub>2</sub> contents in the deposition atmosphere result in the predominant formation of rhombohedral Cr<sub>2</sub>O<sub>3</sub> mixed with fcc CrN.

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## 1. Introduction

The use of thin and hard physically vapour deposited (PVD) coatings in tribological applications has become more and more widespread. However, many industrial applications where coatings could solve tribological problems, e.g. forming tools and different engineering components, use bulk materials (tool steels of the highest hardness, polymers) that cannot withstand temperatures above about 80 to 200 °C due to shape-distortion or loss of hardness. There is, consequently, a high demand for the development of low-temperature PVD processes that are capable of producing coatings with properties corresponding to those of coatings deposited at standard temperatures (typically 400–450 °C). Many questions regarding low-temperature

coating deposition still remain to be answered. For example, low temperature processes may trigger chemical and microstructural changes, resulting in modification of mechanical, tribological and optical properties. Unfortunately, only very limited information on these changes and how they may affect the industrial applicability of such coatings is available.

One of the most promising candidates for low-temperature deposition is the Pulsed Laser Deposition (PLD) technique. By the application of a pulsed laser beam for evaporation of various target materials in inert or reactive low-pressure gas atmospheres a great variety of (tribological, optical, decorative, etc.) coatings with very high adhesion strength to the substrate can be deposited even at room temperature [1,2]. But because of the specific deposition conditions in the PLD technique (high energetic, pulsed plasma combined with low substrate temperatures) new phenomena in the growth of a coating can be obtained especially in room temperature deposition processes [2]. One of these phenomena, the incorporation of high amounts

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of atoms (esp. oxygen) from the deposition gas atmosphere in chromium (Cr) and chromium nitride ( $\text{CrN}_x$ ) coatings will be shown in the current work.

## 2. Experimental

### 2.1. Film deposition

High purity chromium targets (99.9% Cr) were used for the ablation experiments using a pulsed Nd:YAG laser system, which provides four beams of 1064 nm wavelength, 0.6 J pulse energy and 10 ns pulse duration at a repetition rate of 50 Hz [2]. In this multi-spot evaporation system the targets are rotated during the laser irradiation in order to avoid the formation of deep craters. The emitted species were deposited at room temperature (approx. 25 °C) onto steel (AISI 630 HT) and molybdenum substrates mounted parallel to the target surface. Prior to deposition these substrates were mirror-polished and cleaned ultrasonically in pure acetone and ethanol. To provide homogenous film thickness over the whole coated surfaces, the substrates were moved with a relative speed of 5.4 cm s<sup>-1</sup> through the plasma plumes during deposition. The reaction chamber was evacuated before the coating process to pressures below  $2 \times 10^{-3}$  Pa using a pumping unit consisting of a rotary vane pump and a turbo molecular pump. Prior to  $\text{CrN}_x$  deposition pure metallic Cr adhesive interfaces were grown for increasing the adhesion strength of the coatings to the substrates [3,4]. For controlling the gas atmosphere in the recipient the flows of the process gases Ar and  $\text{N}_2$  (Table 1) were adjusted by means of electronic mass flow controllers. Plasma emission spectroscopy was applied to monitor the compositional changes of the laser ablation plasma.

### 2.2. Film characterization

Preliminary chemical analyses of the Cr and  $\text{CrN}_x$  coatings were performed using wavelength disperse spectroscopy (WDS, Microspec WDX-3PC). The phase composition of the coatings was analyzed by an X-ray diffractometer (Bruker AXS D8 Discover) in Bragg-Brentano alignment and  $\text{CuK}\alpha$  radiation.

The film structures were examined by transmission electron microscopy (TEM) of cross-sections of films using a Philips CM20(LaB<sub>6</sub>) transmission electron microscope operating at 200 kV and equipped with a Gatan post column

imaging filter. The sample preparation included standard procedures like cutting, slicing, polishing and finally  $\text{Ar}^+$  ion milling to reach an end-thickness of approximately 100 nm [5]. Besides bright-field imaging also edge signals specific for individual elements were used for chemical imaging by the Gatan imaging filter. A quantification of these element distribution micrographs was performed using the 3-window method. In addition, electron diffraction patterns were taken in the TEM investigations.

## 3. Results and discussion

Preliminary WDS investigations of the chemical compositions of the Cr and  $\text{CrN}_x$  coatings showed nitrogen contents between <1.0 and 33.4 atom.% in dependence on the  $\text{N}_2$  gas flow and the  $\text{N}_2/\text{Ar}$  flow ratio (Table 1). No measurable nitrogen contaminations (<1.0 atom.%) were found in the metallic Cr coating “S1” deposited in pure Ar atmosphere, whereas a nearly linear relation between the  $\text{N}_2$  gas flow and the nitrogen content is obvious for the other samples (“S2”–“S5”). Because of the nearly constant gas pressure during all deposition experiments the scattering of the ablated Cr species with the process gas molecules/atoms ( $\text{N}_2$ , Ar) during the plasma expansion seems to stand in close linear correlation to the amount of chemical reactions between Cr and N in the plasma. But the WDS investigations confirmed apart from N also O atoms in the coatings. Due to the lack of standard materials the oxygen content could not be quantified by WDS. More accurate qualitative information about the distribution of the oxygen atoms in the coatings was obtained in TEM investigations. The chemical imaging by using the edge-signals of the chemical elements Cr, N and O (Fig. 1a–c) give indication to higher contents of the specific element in brighter areas than in darker. The addition of  $\text{N}_2$  to the process gas starting from the interface Cr– $\text{CrN}_x$  increases the N/Cr ratio instantaneously, which is also evident in the quantification of the N/Cr atomic ratio in Fig. 1d. As a result of only interface-near TEM investigations no stabilization of the N/Cr ratio on a distinct value was found in the  $\text{CrN}_x$  coatings, whereas this ratio is nearly constant around 0 in the pure Cr adhesive interface layer. Additionally, the increase of the N content in the coatings goes hand in hand with the decrease of oxygen. Although an O/Cr ratio was not calculated, the loss of brightness with increasing film thickness in the O elemental distribution image (Fig. 1c) confirms that the source of oxygen could only be found in the rest gas in the recipient after evacuation to  $2 \times 10^{-3}$  Pa. The progressive reaction and incorporation of oxygen atoms in the Cr and  $\text{CrN}_x$  coatings as well as in the deposits in the recipient reduces the partial pressure of  $\text{O}_2$  in the chamber. This is evident in the optical emission of the plasma, too. Fig. 2 shows three spectra at the beginning of the CrN coating, just after Cr interface deposition. While the intensity of the whole spectra is slightly decreasing due to covering of the

Table 1  
Applied atmospheres during deposition of the Cr and  $\text{CrN}_x$  coatings and WDS results of their chemical composition

	S1	S2	S3	S4	S5
$\text{N}_2$ gas flow [sccm]	0	5	10	20	25
Ar gas flow [sccm]	30	25	20	5	0
Flow ratio $\text{N}_2/\text{Ar}$	0	0.2	0.5	4	–
N content of coating [atom.%]	<1.0	22.9	24.9	30.5	33.4

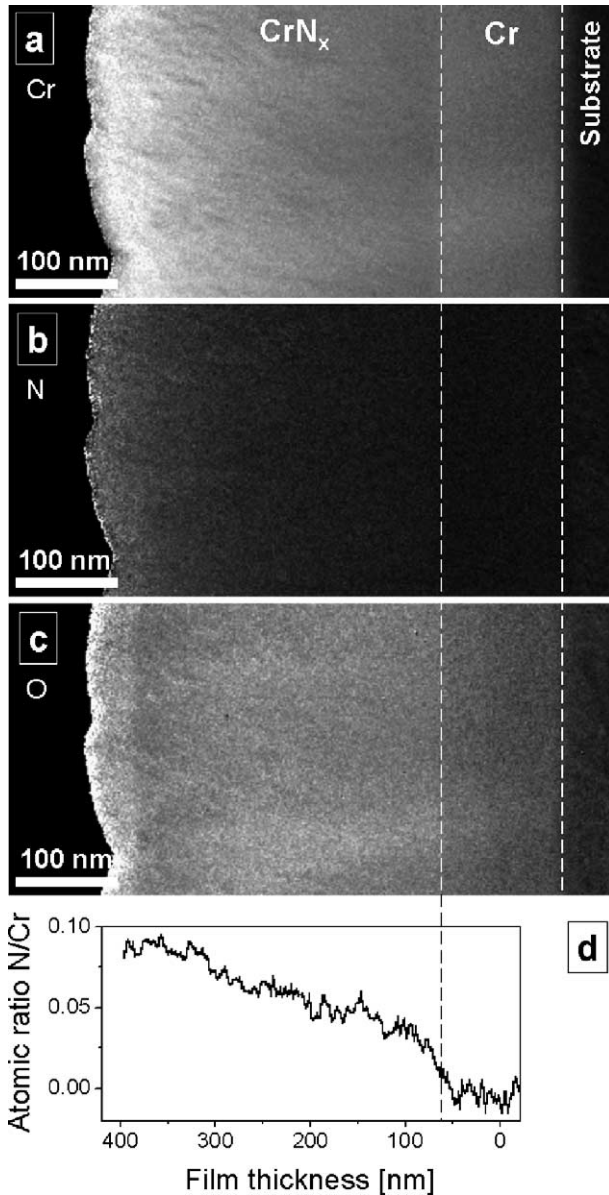


Fig. 1. Chemical TEM imaging of (a) Cr, (b) N and (c) O elemental distribution in the Cr interlayer and the CrN<sub>x</sub> layer of the coating “S5”. (d) Quantified atomic ratio N/Cr dependent on the film thickness of the cross-sections investigated.

protection window during deposition, the single ionic oxygen double-peak (OII) at 372.7 and 374.9 nm is drastically diminished. Hence, the amount of reactions between Cr and N species in the plasma is increasing. Comparing the energies for fission of O<sub>2</sub> and N<sub>2</sub> molecules to atoms or ions (O<sup>g</sup>, N<sup>g</sup>) and for the formation of Cr–N and Cr–O compounds, it is evident, that (1) the fission of O<sub>2</sub> demands less energy than N<sub>2</sub> and (2) the reactions occurring in the laser plasma between evaporated gaseous Cr and O atoms (e.g.  $2\text{Cr}^g + 3\text{O}^g \rightarrow \text{Cr}_2\text{O}_3^s$ ) are favored to that with N (e.g.  $2\text{Cr}^g + \text{N}^g \rightarrow \text{CrN}^s$ ). In contrast, reactions on the substrate surface between physisorbed molecular N<sub>2</sub> and O<sub>2</sub> and Cr are very improbable.

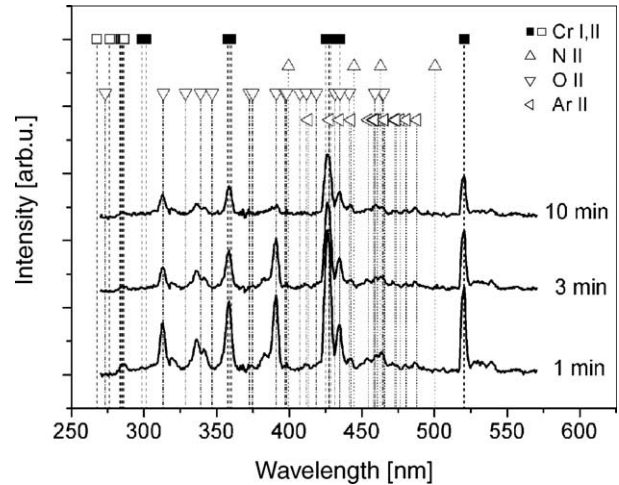


Fig. 2. Plasma emission spectra of the CrN deposition in dependency on the time of CrN layer growth.

The incorporation of oxygen atoms in the coatings leads to strong influences on the growth conditions of the coatings. Evidences therefore can be observed in the XRD spectra taken from the as-deposited coatings in Fig. 3. Except for the reflections of the Mo substrates three distinct peaks were found.

For the coatings deposited in atmospheres of the highest Ar gas flows (lowest N contents) the (1 1 1) reflection appears at a diffraction angle of about 44°. Because of the very low N content of the nearly pure Cr coating “S1” this peak can only be assigned to the bcc  $\alpha$ -Cr phase. The peak is shifted in all three coatings (“S1”, “S2” and “S3”), in which it is evident, to higher diffraction angles  $2\theta$  indicating lattice constants significantly higher than for pure  $\alpha$ -Cr. Due to the increase of the peak shift from the standard position of  $\alpha$ -Cr and the decrease of peak intensity in the coatings “S2” and “S3”, grown in atmospheres containing N<sub>2</sub>, the shift seems to be caused by the incorporation of small atoms like O (or Ar) on lattice sites

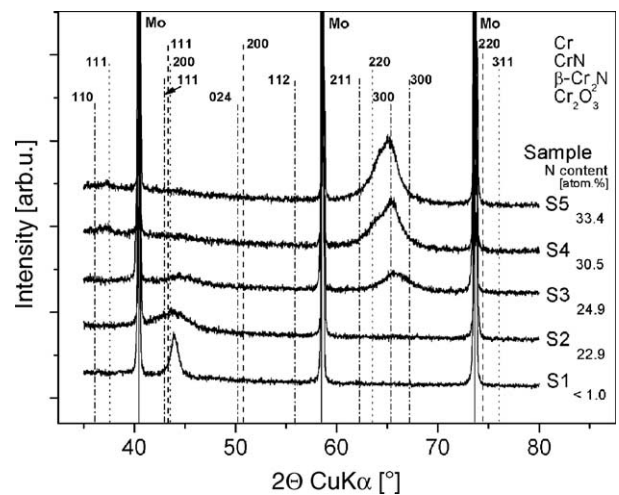


Fig. 3. XRD spectra of the Cr and CrN<sub>x</sub> coatings. The standard positions of the diffraction peaks are indicated for Cr, CrN,  $\beta$ -Cr<sub>2</sub>N and Cr<sub>2</sub>O<sub>3</sub> [6].



of Cr atoms. The higher the content of such lattice defects the higher lattice strains are caused, resulting in a decrease of crystallinity of the bcc  $\alpha$ -Cr.

This loss of crystallinity of  $\alpha$ -Cr goes together with an arising peak at about  $65^\circ$ . A comparison of the center position of this peak with different CrN phases (hcp  $\beta$ -Cr<sub>2</sub>N or fcc CrN) lead to peak shifts of up to  $4^\circ$ , which is implausible for CrN coatings. However, the (3 0 0) reflection of rhombohedral Cr<sub>2</sub>O<sub>3</sub> gives a good correspondence to this peak. The peak is shifted to lower diffraction angles in the XRD spectra of the coatings “S3”, “S4” and “S5” and becomes broader at increased nitrogen contents. Furthermore, this reflection becomes unsymmetrical for the coatings “S4” and “S5”. Combined with the appearance of a low-intensity peak near  $37.5^\circ$ , which can be assigned to (1 1 1) fcc CrN, the peak broadening and asymmetry of the (3 0 0) peak seems to be caused by the appearance of the (2 2 0) CrN peak.

Thus, the microstructure of the CrN coatings “S3”, “S4” and “S5” is two-phased: either  $\alpha$ -Cr and Cr<sub>2</sub>O<sub>3</sub> or Cr<sub>2</sub>O<sub>3</sub> and CrN. Normally, CrN and Cr<sub>2</sub>N phases are found in two-phase CrN coatings deposited at low temperatures [3,7,8]. Two-phase structures of CrN and Cr<sub>2</sub>O<sub>3</sub> are usually characteristic for coatings deposited by magnetron sputtering in atmospheres of O<sub>2</sub>/N<sub>2</sub> gas flow ratios  $>0.33$  [9]. Such high oxygen contents are not plausible in the deposition atmosphere applied in the current investigations, which is consisting of the rest gas after evacuation to  $2 \times 10^{-5}$  mbar and the process gas of about 1000 times higher pressures. Thus, it is evident by the much higher degree of oxygen contaminations that the high-energetic pulsed-plasma conditions of the PLD technique highly promote the oxygen trapping. Results of PLD CrN<sub>x</sub>O<sub>y</sub> coatings by Suzuki et al. [10] gives further confirmation of this theory, who also found high contents ( $>40$  atom.%) of oxygen in the deposits. In this work the oxygen incorporated during film growth at  $400^\circ\text{C}$  originates from the rest gas atmosphere after evacuation too, but it is incorporated in the fcc CrN phase and does not lead to the formation of the Cr<sub>2</sub>O<sub>3</sub> phase.

It is further well known that in thermal equilibrium conditions neither Cr, Cr<sub>2</sub>O<sub>3</sub> nor CrN phases can dissolve even low contents of foreign elements like N and O [3]. Thus, phase separation and two-phase structures are most expectable. In the current work the high-energetic plasma of the PLD technique in combination with the low temperatures of the substrates ( $25^\circ\text{C}$ ) causes a solution of O atoms in the metallic  $\alpha$ -Cr and a solution of N atoms in the Cr<sub>2</sub>O<sub>3</sub> lattice, which is evident by the broad peaks and large peak-shifts from the standard position of unstressed lattices. Thus, the pulsed plasma conditions result in the missing of long-distance diffusion processes (some nm distances) at the low substrate temperatures and to the strong disequilibria state in the coating structures [11].

#### 4. Conclusions

The current paper revealed a tendency to oxygen trapping in chromium (Cr) and chromium nitride (CrN<sub>x</sub>) coatings grown by the room temperature Pulsed Laser Deposition (PLD) technique. The oxygen atoms lead to tensile stresses of the crystal lattices of e.g.  $\alpha$ -Cr, and to the formation of Cr<sub>2</sub>O<sub>3</sub> phases at high N<sub>2</sub> contents in the deposition atmosphere. The amount of oxygen entrapped in the coatings is decreasing in thicker films indicating the source of oxygen as the rest gas after evacuation of the recipient to end pressures of  $2 \times 10^{-3}$  Pa prior coating. The high contamination with oxygen atoms results in combination with the high energetic pulsed-plasma of the PLD technique in very fine-grained coating structures.

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