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Thermal behaviour of chromium nitride/titanium–titanium carbonitride multilayers

P. Angerer [a,*], J.M. Lackner [b], M. Wiessner [a], G.A. Maier [a], L. Major [c]

[a] Materials Center Leoben Forschung GmbH, 8700 Leoben, Austria
[b] JOANNEUM RESEARCH Forschungsgesellschaft mbH, Institute for Surface Technologies and Photonics, Functional Surfaces, 8712 Niklasdorf, Austria
[c] Institute of Metallurgy and Materials Science Polish Academy of Sciences, 25 Reymonta Street, 30-059 Krakow, Poland

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ABSTRACT

Chromium nitride/titanium–titanium carbonitride multilayers composed of a 40 nm Cr interface followed by a 4.4 μm thick Cr_2N layer, a 150 nm thick Ti layer, and a 1 μm thick TiC_xN_y top layer were deposited on silicon wafers by magnetron sputtering. The structural changes and the phase content changes of these multilayer samples were studied by means of high-temperature in-situ X-ray diffraction experiments at temperatures up to 550 °C. The lattice constants of the Cr phase as well as the Ti phase display an aberrant expansion behaviour during these experiments which is influenced by the defect structure, a nitrogen incorporation, and residual stress in the layers. The results were compared with structural data obtained by ex-situ transmission electron microscopy investigations of pristine and heated material, revealing phase separation and strong diffusion phenomena.

1. Introduction

Chromium nitride (CrN_x) coatings, deposited by physical vapour deposition methods, are well-known wear protecting materials in various technical applications (automotive, mechanical engineering, decorative, corrosion protection) due to the combination of high hardness, corrosion resistance, and thermal resistance [1]. However, these coatings lack low friction properties, which are necessary in sliding operations to decrease frictional and wear losses for extending the lifetime under e.g. sliding conditions. Applying low friction top layers of carbon containing materials is a candidate for such improvements [2]. This work focusses on such a multilayer system, deposited by magnetron sputtering, and describes the microstructural changes due to elevated temperatures, simulated by thermal annealing and in-situ high temperature X-ray diffraction (XRD) and ex-situ transmission electron microscopy (TEM). For the relation between structure and tribological properties of chromium nitride coatings, the paper of Rebholz and coworkers should be consulted [3]. Structural and chemical properties of chromium nitride and carbide layers were investigated in [4] whilst the works [5] and [6] are more focussed on structural and mechanical properties of related carbonitride materials. In [7] the morphology and the corrosion on similar layers deposited on aluminium alloy substrates were investigated.

2. Experimental details

Deposition of coating was performed using magnetron sputtering on boron doped, polished, non-oxidized (1 0 0) silicon wafer substrates. Before deposition, the substrates were first cleaned with acetone and ethanol, dried, and mounted on the substrate carousel. Afterwards, the vacuum chamber was pumped down to start pressure (1×10^{-3} Pa) and chemical activation started in oxygen–argon atmosphere (to remove organic contaminations) and in argon atmosphere to etch the oxide layer, both by using an anode layer ion source [8]. Unbalanced magnetron sputtering was afterwards used to deposit the multilayer structure at maximum 70 °C substrate temperature consisting of a ~40 nm thick pure chromium (Cr) interface layer, continued by a ~4.4 μm thick chromium nitride (Cr_2N) layer and a ~150 nm thick pure titanium (Ti) layer and finalized with a ~1 μm thick titanium carbonitride (TiC_xN_y) top layer [2]. The deposition of all chromium and titanium layers was done from high purity chromium (99.99%, manufactured by RHP Technology GmbH, Seibersdorf, Austria) and titanium (99.99%, supplied by EuroTitan GmbH, Solingen, Germany) targets, respectively, in a four-cathode, industrially scaled magnetron sputter batch coater at JOANNEUM RESEARCH (for details compare [9,10]). Direct current (DC) sputtering in inert argon and reactive argon–nitrogen atmospheres was used for Cr and Cr_2N deposition (Ar and N_2: 99.999% purity, manufactured by Linde Gas, Stadl-Paura, Austria), respectively. In contrast, Ti and TiC_xN_y were sputtered in a pulsed DC discharge (80 kHz frequency, 1 μs pulse duration) in inert and argon–nitrogen–acetylene (C_2H_2, 99.99% purity, manufactured by Linde Gas, Stadl-Paura, Austria),

* Corresponding author. Tel.: +43 3842 45922-25; fax: +43 3842 45922-500.
E-mail address: paul.angerer@mcl.at (P. Angerer).

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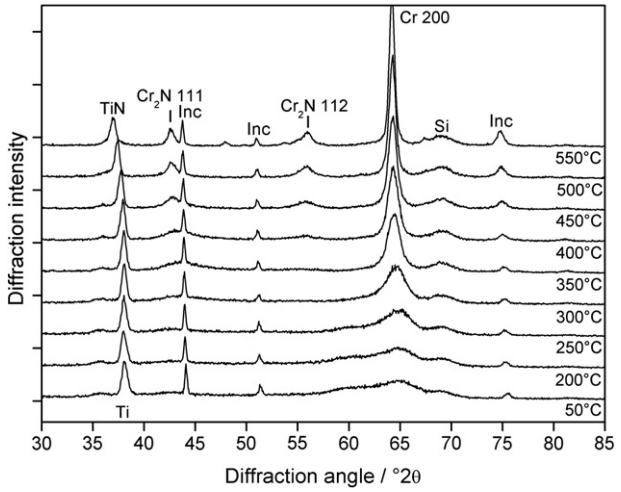

Fig. 1. Stacked plot of the diffraction data recorded during the HT-XRD in-situ experiments at various temperatures. The peaks assigned to the phases Cr, Cr_2N, Ti, and TiN are indicated. "Inc" denotes diffraction peaks that originate from the Inconel sample holding clamps.

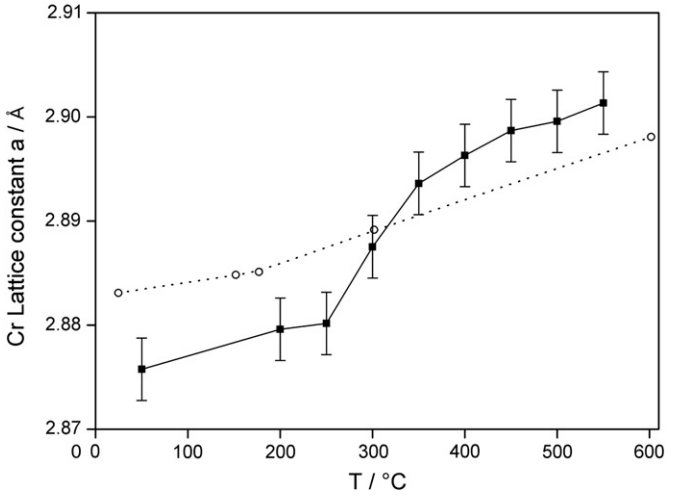

Fig. 3. Development of the lattice constant a of the Cr phase calculated from diffraction data of the Cr (2 0 0) maximum recorded during the HT-XRD experiment (open circles denote corresponding reference values).

respectively. −50 V bias voltage was applied during deposition on the continuously rotated substrates.

3. Characterization techniques

The characterization by means of the XRD method in respect to phase composition, lattice parameters, crystallite size, crystallographic texture (preferred orientation), and residual stress was conducted on a D8 Discover diffractometer (Bruker AXS, Germany) in parallel beam geometry (40 kV, 35 mA, Cu Kα radiation). This device is equipped with a Sol-X energy dispersive detector, an open (90°) Eulerian cradle, and a polycapillary collimator. For the in-situ high temperature diffraction measurements (HT-XRD) a domed high-temperature stage DHS900 manufactured by Paar, Austria [11] was attached. The heating rate was 1 °C/s, the subsequent XRD scans were then conducted under isothermal conditions (at 50 °C, 200 °C, and then in constant steps of $\Delta T = 50$ °C up to 550 °C). Each scan for the phase analysis during the HT-XRD series was obtained in the range 20°–130° 2θ with a step size of 0.05° and a counting time of 3 s/step. All HT-XRD experiments were conducted under constant N_2 flux. The texture characterization (i.e. pole figure determination) was performed in the same diffraction geometry. Further specific measurement parameters or the texture determination are reported in our paper [8]. For the determination of the position, integrated area, and full width at half maximum (FWHM) of specific diffraction maxima, the TOPAS 4.2 Software by Bruker AXS, Germany was used. The evaluation of the pole figure measurements and the corresponding calculations was conducted using the LABOTEX 3.0.22 texture analysis software by LaboSoft, Poland. The HT-XRD stress determination was made by means of the side inclination method on the DHS900 stage as well. The stress calculations were performed according to the conventional $\sin^2\psi$-method (with a tilt angle $\psi \leq 24°$) [12] using the Stress32 software, version 1.1 also by Bruker AXS, assuming a Young's modulus $E = 283$ GPa and a corresponding Poisson's number $\nu = 0.21$ for the Cr phase in [3 1 0] direction according to Voigt's model [13]. A high temperature in-situ XRD study of the residual stress development in CrN hard coatings up to 800 °C was presented by Kirchlechner and collaborators [14].

The characterization by high resolution TEM was conducted on a TECNAI G2 F20 instrument with a 200 kV FEG in bright field. Electron diffraction patterns and high resolution (HR) techniques were applied for phase analysis. Thin foils for TEM investigations were prepared by the focused ion beam technique (FIB) with gallium ions for milling (Quanta 200 3D DualBeam microscope equipped with in-situ OmniProbe micromanipulator).

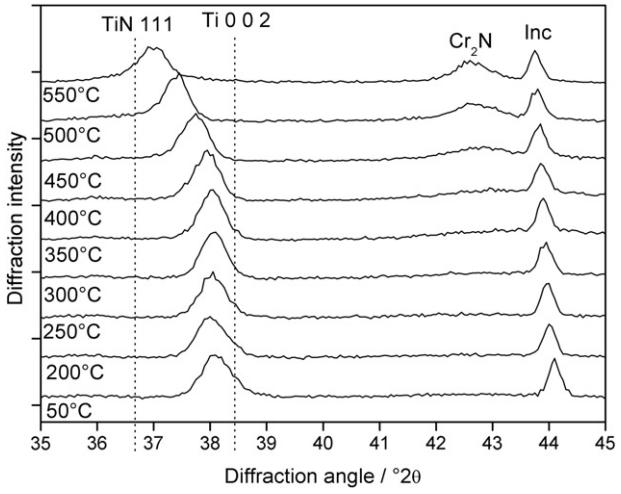

Fig. 2. Stacked plot of the data recorded during the HT-XRD experiment focussed on the range of 35–45° 2θ. The changes of the diffraction angle of the diffraction maximum related to the Ti–N phase are obvious. The vertical dotted lines refer to the reference values (ICDD-PDF) for the indicated maxima at room temperature.

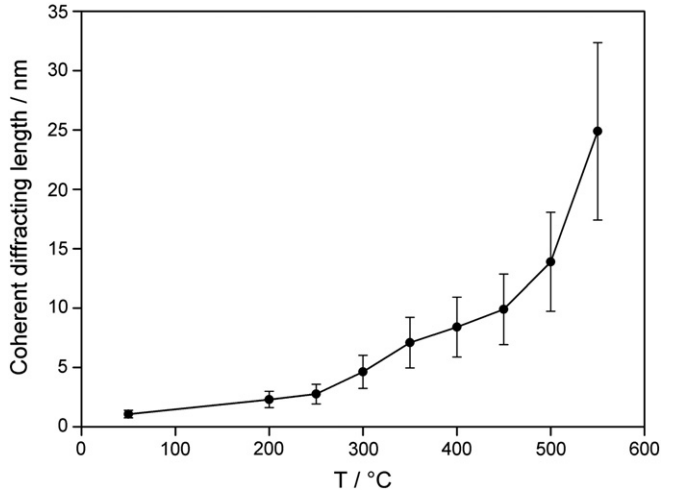

Fig. 4. Development of the coherent diffracting length of the Cr phase calculated from peak width data of the Cr (2 0 0) maximum during the HT-XRD experiment.