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Microstructure and defect characterization at interfaces in TiN/CrN multilayer coatings

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ABSTRACT

Microstructures of TiN/CrN multilayer coatings deposited on austenite steel (Cr Ni 18 8) by pulsed laser deposition (PLD) are characterized using transmission electron microscopy while their mechanical properties were assessed in a ball-on-disk test. All coatings have the same total thickness of about 1 μm. The individual layers show a highly defective columnar structure, which is characterized by conventional electron microscopy (TEM) as well as by high resolution TEM. These techniques, combined with measurements of the local chemical composition through EDS prove that PLD allows to produce fully separated CrN and TiN layers. The friction, and consequently the wear, are lowered by increasing the total number of layers in the coating.

1. Introduction

Hard and corrosion resistant coatings are used to reduce the wear of tools and as a consequence to increase their lifetime. The most common hard coatings are based on transition metal nitrides such as TiN or CrN. Their deposition either Chemical Vapor Deposition (CVD) or Physical Vapor Deposition (PVD), are well established techniques in industry at present time. Titanium nitride exhibits, besides low wear and erosion, also a good heat resistance and a low friction coefficient; it is therefore widely applied in different fields as an engineering ceramic, e.g. as a cutting tool coating [1,2]. Chromium nitride on the other hand has an excellent high temperature stability and is often used in applications where not only hard but also oxidation and corrosion resistant coatings are required [3,4].

The PVD coatings are characterized by a strongly defective microstructure and they exhibit higher hardness than bulk material depending on the deposition condition. These coatings can be deposited as multilayers or nano composites [5,6]. Especially, the multilayer PVD coatings have been a subject of great interest in the last decade [7]. Usually they present both, higher hardness and toughness as compared to the monolayered ones. The multilayer coatings can be divided into two groups, i.e. coatings built from layers of materials with:

- strongly different unit cell i.e. forming non-coherent interfaces between the layers.
- similar unit cell size and structure, allowing the formation of partially or fully coherent interfaces.

The growth defects and stress resulting in the formation of locally coherent interfaces are the most important factors responsible for an increase in the coating strength. However, the experimental evidence of lowering the wear with an increased defect density is still scarce.

The aim of the present paper is, except from a compositional study, an atomic scale analysis of the defects at the interfaces as well as within the individual layers in the multilayer TiN/CrN coatings. The structural results are discussed in relation to the micromechanical properties.

2. Experimental procedures

2.1. Coatings deposition

High purity titanium as well as chromium targets (99.9 at.% Ti, 99.9at.% Cr) were used for ablation experiments using a pulsed Nd:YAG laser system. The deposition process is described in detail in [8]. Deposition parameters are presented in Table 1. In all cases a TiN buffer layer was first deposited in order to increase the coating adhesion to the substrate (CrN layers are characterized by weaker adhesion).

2.2. Coating characterization

A TECNAI G2 F20-TWIN™ (200 kV) and a JEOL EX 4000 (400 kV) transmission electron microscope were used for the microstructural characterization. Thin foils from cross-section were prepared using,

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Table 1
Deposition parameters of multilayer coatings TiN/CrN

Number of layers	Type of layers	Target	Time of the deposition	Gas flow	Total coating thickness (μm)
2	TiN/CrN	Ti Cr	45′TiN+60′CrN	45′30 sccm N_2; 60′30 sccm N_2	1
8	4×TiN/CrN	Ti Cr	4×(11′9″TiN+ 15′CrN)	4×(11.15′30 sccm N_2; 15′ sccmN_2)	1
32	16×TiN/CrN	Ti Cr	16×(2′29″TiN+ 3′45″CrN)	16×(2′29″30 sccm N_2; 3′45″30 sccm N_2)	1

either a FEI Dual Beam™ FIB or a TriPod followed by argon ion milling. In order to analyze the defects in the layers and at the interfaces between them, Bragg filtered High Resolution TEM recordings (HRTEM) were used [10]. Bragg filtering is obtained by placing a mask around the spots $\pm\vec{g}$ in the Fourier transform of the image and subsequently taking the inverse Fourier transform of only the selected spots. This filtering results in an image showing only the crystal planes corresponding with the selected $\vec{g}$, and allows in a more easy way to identify dislocations on the HRTEM images.

Chemical analysis was performed using energy dispersive X-ray spectroscopy (EDS) in order to investigate the spatial separation of chromium and titanium based layers.

The adhesion was examined by a scratch test (Rockwell HRC penetrator). The scratch length was 2 mm on which the load increased linearly from 0.03 N up to 30 N. Wear was studied using a ball-on-disk test.

3. Results and discussion

The present examination was initiated for a two-layered coating. The diffraction patterns obtained using a parallel beam, (i.e. in selected area diffraction) allowed to confirm the presence of only cubic phases (the unit cell dimensions of both components are very similar). The measured d-spacings from the ring like diffraction patterns are match well with the values for the bulk material. Since all rings were identified with the TiN and CrN cubic phase, these measurements helped to exclude the presence of significant impurities of titanium or chromium oxide [9]. The CrN diffraction pattern is less blurred and contains more spots than the TiN one; this is due to a much smaller size and more random orientation of the crystallites in the latter. The TiN and CrN ring type diffraction patterns are shown in Fig. 1.

Both layers, CrN and TiN, are built up of columnar crystallites; this can be clearly seen in Fig. 1. The diameter of the TiN columns is significantly smaller than that of the CrN ones, i.e. they are in the range of ~25 nm and ~40 nm respectively. EDS analysis and the corresponding imaging proved the spatial separation of chromium and titanium based layers, as shown in Fig. 2. The results confirm that there has been no chemical reaction at the interface and that the formation process is non-diffusive.

Coatings containing a larger number of layers, like 8 and 32, very much confirm the characteristics of the bilayers, i.e. finer TiN and coarser CrN crystallites (Fig. 3). Careful microstructure observations of coatings containing a larger number of layers reveal that in all cases crystallites in the buffer layer are much smaller than in the following layers of the same nature.

The analysis of dislocations was performed using HRTEM. The defects at interfaces and in the interior of the grains were analyzed separately. HRTEM images not always show a clear interface between TiN and CrN due to an overlap between TiN and CrN grains or the fact that only one of the grains is oriented along a proper zone axis. A situation where both structures show a two dimensional resolution is presented in Fig. 4. By visualizing one set of crystal planes using Bragg

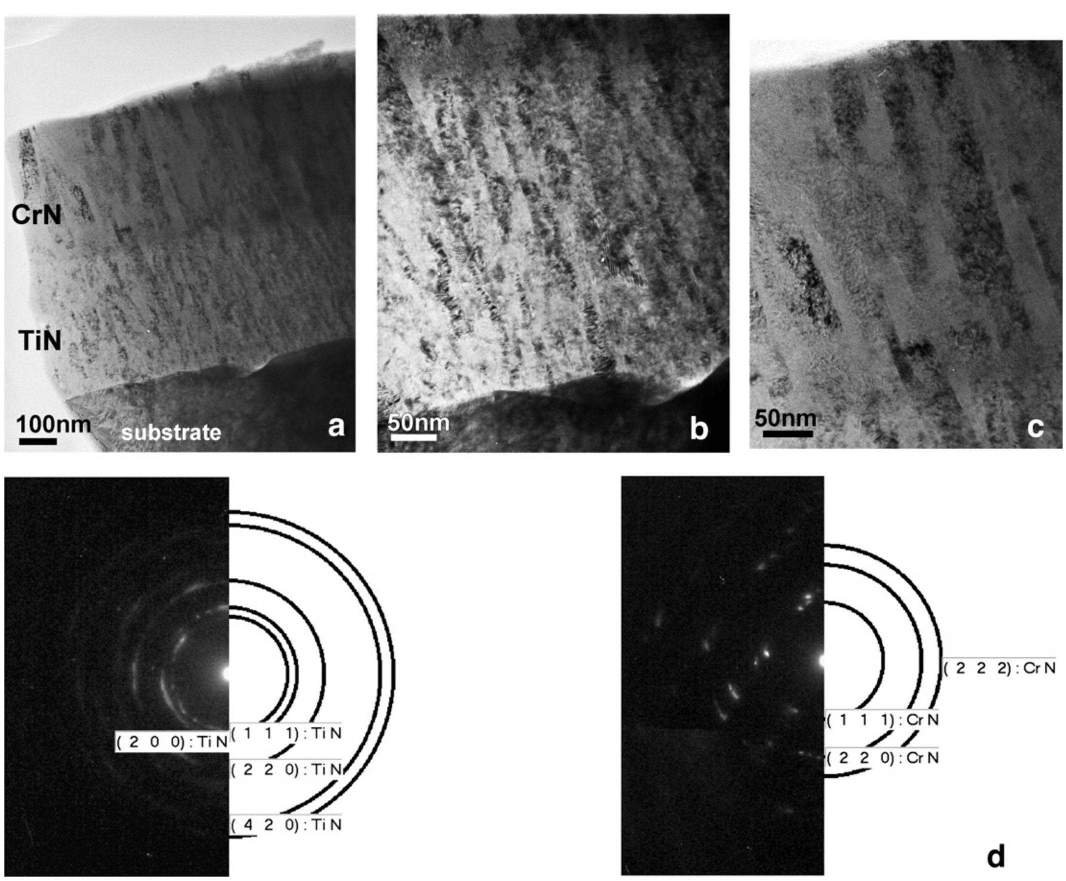

Fig. 1. a) Microstructure of the cross-section of a two-layered TiN/CrN coating; b) TiN layer; c) CrN layer; d) diffraction patterns of TiN and CrN coatings.