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Crystallographic aspects related to advanced tribological multilayers of Cr/CrN and Ti/TiN types produced by pulsed laser deposition (PLD)

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Abstract

The microstructure of the Cr/CrN and Ti/TiN multilayers coatings deposited with the pulsed laser deposition (PLD) technique was studied using transmission electron microscope Philips CM20 TWIN (200 kV). It was found that the metallic buffer layers are characterized by the smallest columnar crystallite size and the highest defect density; this might rise their hardness but compromise the coating adhesion. The intermediate metallic layers showed a larger and less defected columnar structure as compared with the nitride layers, what should improve the coatings toughness. The scratch test performed with a Rockwell penetrator of 200 μm diameter loaded from 0.03 N up to 20 N indicated that the switching from a single layer to a multilayered metal/nitride coating of the same thickness improved the resistance to scratch test in case of Ti/TiN from 16.4 N for a TiN single layered to 22.9 N for a 32 layered coating and Cr/CrN from 4.4 N for a CrN single layered to 6.6 for a 32 layered ones.

Keywords: Multilayers; Pulsed laser; Microstructure; Tribology

1. Introduction

Titanium nitride with a characteristic gold color that can be deposited using different techniques is still the most popular hard coating for industry [1]. However, requirements to withstand an aggressive environment at elevated temperatures have resulted in switching interest to chromium nitride coatings, which form a surface passive oxide layer stopping further degradation [1–7].

The majority of commercial TiN tool coatings even now consist of a single layer of deposited material. However, it was shown recently that a stack of adequately thin layers may have a much higher hardness than either one separately [8]. This gain in hardness is achieved through stress accumulation at the layer interfaces and therefore some softer buffer layer between the bottom of such stack and substrate should be added to prevent its delamination [9,10]. Placing softer layers in between hard ones may arrest the crack propagation and increase the toughness of the coating. The rise in coating hardness matched with a control of their stress level should result in a markedly improved wear resistance of the tool [11].

Most of the established coating deposition techniques require or result in substrate heating. However, some temperature

Table 1

No. of layers	Target	Deposition atmosphere and time
4	Cr	Vacuum/∼ 1′ + 2 × (Ar 30 sccm/37.5′ followed by N_2 30 sccm/30′)
8	Cr	Vacuum/∼ 1′ + 2 × (Ar 30 sccm f/18.75′ followed by N_2 30 sccm/15′)
32	Cr	Vacuum/∼ 1′ + 2 × (Ar 30 sccm/4.7′ followed by N_2 30 sccm/3.75′)
4	Ti	Vacuum/∼ 1′ + 2 × (Ar 30 sccm/30.30′ followed by N_2 30 sccm/22.50′)
8	Ti	Vacuum/∼ 1′ + 2 × (Ar 30 sccm/15.30′ followed by N_2 30 sccm/11.25′)
32	Ti	Vacuum/∼ 1′ + 2 × (Ar 30 sccm/3.75′ followed by N_2 30 sccm/2.30′)

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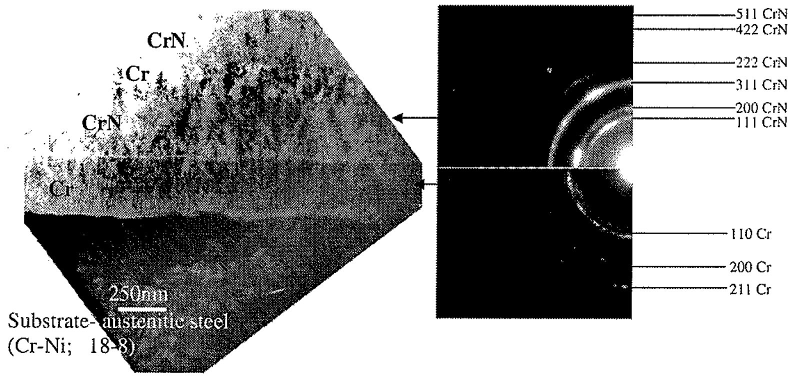

Fig. 1. TEM microstructure of the Cr/CrN 4 layers deposited on the austenitic substrate.

sensitive materials like machine parts have to avoid such exposure and therefore techniques like pulsed laser deposition (PLD), which allows to produce coatings with a good adhesion also at room temperature, should be applied [12–16].

The aim of the present project is to investigate the possibilities of deposition of multilayer Ti/TiN or Cr/CrN coatings using the PLD technique, analyze their microstructure and test some tribological properties.

2. Experimental procedures

2.1. Coatings deposition conditions

Multilayer coatings based on Cr/CrN as well as Ti/TiN have been deposited on an austenite substrate. High purity targets (99.9% Ti and 99.9% Cr) were used for ablation experiments with a pulsed Nd:YAG laser system operating at 1064 nm wavelength, 0.6 J pulse energy and 10 ns pulse duration at a repetition rate of 50 Hz. The targets were rotated during the laser irradiation in order to avoid the formation of deep craters. The emitted species were deposited at room temperature onto austenitic steel (AISI 301, DIN CrNi 18 8) substrates mounted parallel to the target surface. To provide a homogenous film thickness over the whole coated surface, the substrates were moved with a relative speed of 5.4 cm/s through the plasma plumes during deposition. The Cr as well as the Ti interface layers were deposited at Ar atmosphere (99.99), while for deposition of the nitrides N_2 was blown (99.99).

2.2. Coating design

The analyzed coating consisted of 4, 8 and 32 Cr/CrN or Ti/TiN layers, respectively. They were deposited using the same approach, i.e. the titanium or chromium ablation was started under a low pressure of argon atmosphere and next at intervals corresponding to the planned nitride layers, nitrogen was blown as specified in Table 1.

2.3. Thin foil preparation and observation conditions

Philips CM20 (200 kV) as well as JEOL EX4000 (400 kV) microscopes were used for the microstructure investigation of a

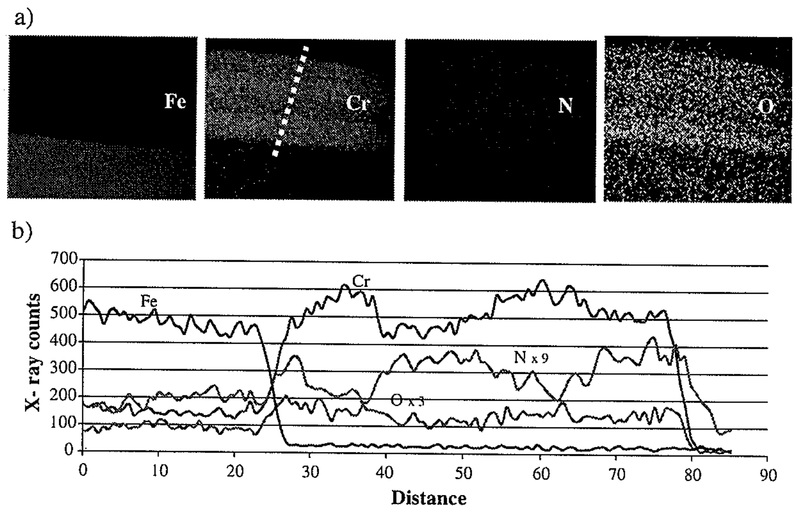

Fig. 2. EDS maps of distribution of Cr, N, O and Fe (a) and line scan as marked on Cr map (nitrogen and oxygen signal was multiplied nine and three times, respectively).

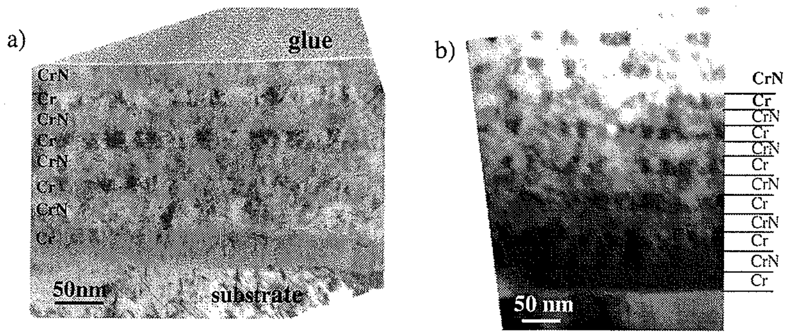

Fig. 3. TEM image of (a) 8 and (b) 32 layered Cr/CrN deposited onto the austenitic substrate.

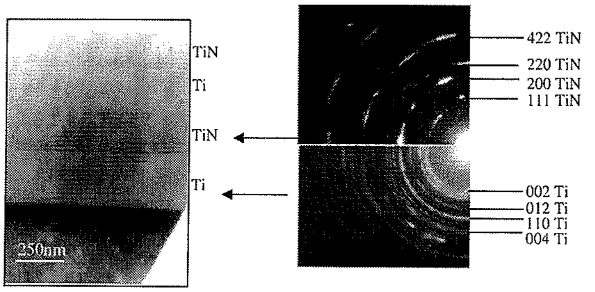

Fig. 4. TEM image of the 4 layered Ti/TiN deposited on the austenitic substrate.

cross-section of the coatings. Energy dispersive spectroscopy (EDS Phoenix EDAX) was used for the local chemical analysis. Focus ion beam (FIB) or "tripod" polishing followed by an Ar^+ ion milling has been applied for thin foils preparation.

2.4. Coating mechanical testing

The adhesion was tested by a scratch test using a Rockwell penetrator (diameter = 200 μm). The scratch length was 2 mm. A linear increase of the load from 0.03 N up to 30 N was applied.

3. Results

3.1. Microstructure observations

The Cr/CrN 4 layers coatings deposited using a Cr target at varying Ar and N_2 pressures were showing a clearly defined layered structure (Fig. 1). All layers were characterized by a highly defected columnar microstructure. The Cr intermediate layer was built up of slightly coarser columnar crystallites as compared to the CrN or Cr buffer. The selected area diffraction patterns, acquired predominantly from the buffer and the first CrN layer, contain rings in good agreement with the Cr and CrN lattice spacing, respectively (in case of such thin layers, for which the size of aperture is comparable with the layer thickness, some signal mixing have to be accepted). The EDS mapping (Fig. 2a) not only confirmed that layers depleted in chromium contain nitrogen, but also indicated a raised of the oxygen level in the buffer layer. The line scan (taken along a line marked in Fig. 2a) (Fig. 2b) acquired at a longer acquisition time than the pixels in the map showed a higher sensitivity and the presence of a chromium gradient in the buffer layer.

The coatings consisting of more Cr and CrN layers (8 and 32 layers) generally a presented similar microstructure as the one built of 4 layers (Fig. 3). Their common most characteristic feature was a much smaller width of the columnar crystallites in the buffer layer. The decreasing thickness of the layers in the multilayer coating resulted in seemingly coarser microstructure than in the coatings having a lower number of layers. It should also be pointed out that in thin regions all Cr layers were showing a stronger sharper diffraction contrast, i.e. larger difference between black and white levels, than the CrN layers characterized by fluctuating diffuse grayish changes. A mass thickness effect should be excluded, as the metal has a higher density than its nitride and thin foils prepared by the focused ion beam (FIB) technique have roughly parallel sides. Therefore, the observed higher contrast levels in Cr layers as compared to CrN probably results from a less defected structure. This effect is much welcome in case of layers, which should arrest crack propagation and toughen the final coating.

Switching from ablation of a chromium to a titanium target at alternating argon and nitrogen pressure allowed to produce coatings of a varying number of titanium and titanium nitride

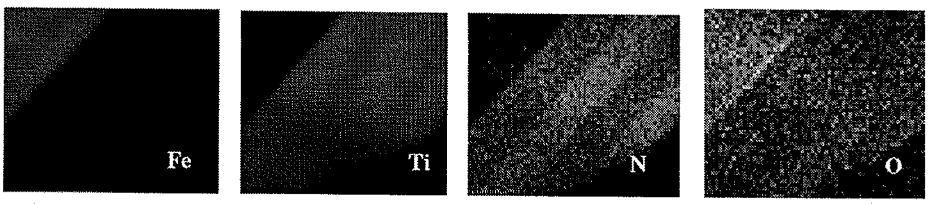

Fig. 5. EDS maps of Cr, N, O and Fe distribution, respectively.

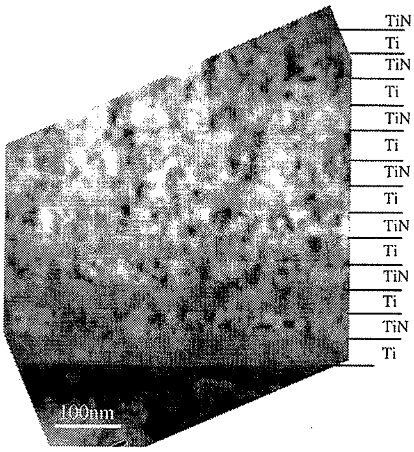

Fig. 6. TEM image of the 32 layered Ti/TiN deposited on the austenitic substrate.

layers, as confirmed by selected area diffraction (Fig. 4) As in the case of Cr/CrN multilayered coatings, both 4 and 32 layered Ti/TiN coatings have been investigated. These observations were performed relying on thicker areas of the thin foils and therefore they show alternating lighter and darker diffuse contrast proper for less and more dense Ti and TiN layers, respectively. The finer nature of the crystallites in the first Ti layer, i.e. in the buffer, as compared with the next layers is however clearly visible in their diffraction patterns, which shows fine and nearly continuous rings, while the others present much more and spotty coarser rings.

The maps of local chemical composition obtained using energy dispersive X-ray spectroscopy (EDS) confirmed a slight depletion of titanium in every second layer accompanied by an increased nitrogen level (Fig. 5). The presence of a weak nitrogen signal from the nominal titanium layers might result from the surface layer formed during the final stages of sample preparation. Again, a quite strong concentration of oxygen at the substrate–buffer interface was noted.

The Ti/TiN coatings built of a higher number of layers showed a similar microstructure as those of the Cr/CrN coatings, i.e. very fine columnar crystallites in the buffer layer and a less defected structure of the metallic interlayers (Fig. 6).

3.2. Mechanical tests

The scratch test was used to asses the mechanical properties of multilayered Cr/CrN and Ti/TiN type coatings. Additionally,

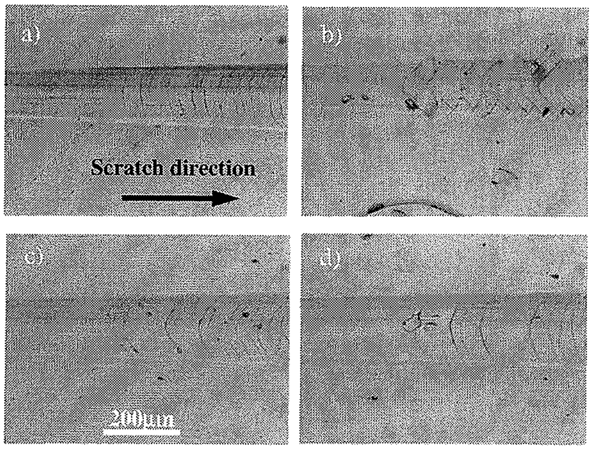

Fig. 7. Images of scratch path up to critical load L_c (a) Cr: single layer, (b) CrN: single layer, (c) Cr/CrN: 4 layers and (d) Cr/CrN: 32 layers.

as a reference single layer coatings of these materials were analyzed. The contact of the scratch indenter with the single Cr layer under a small, i.e. ~5 N load resulted in the formation of very small unconformal type buckling cracks within the scratch track. Only the application of much higher loads, i.e. above 20 N, causes cracks at the edges of the scratch track, which however remain limited the vicinity of the track area even up to 30 N. The load under which the side cracks started to develop was defined as the critical load L_c. Generally, that type of wear traces indicates a very good adhesion of the coating with the substrate.

The scratch test performed on the single CrN layer caused the formation of a net of extensive chevron cracks already at 4 N and, therefore, this value of the load was accepted as L_c. A rise of the load up to 10 N caused total destruction of the coating. The Cr/CrN multilayers subjected to the same test showed intermediate resistance to cracking under the indenter as compared to Cr and CrN coatings. The first unconformal type of buckling cracks on the wear track appeared under the load of 6 N, which was taken as the L_c. Under higher value of the applied load, i.e. from 9 to 13 N, conformal type buckling cracks developed. The behavior of the Cr/CrN 2 layers was a little different. Two kinds of cracks (unconformal and conformal) appeared at the same time. The results are presented in the Table 2 and Fig. 7.

The scratch test has also been performed on the Ti/TiN series of coatings built from 1 to 32 layers (as it was in the case of Cr/CrN based multilayer materials).

Table 2

Sample	Max. load [N]	L_c [N]
Cr	30	5/19.5
CrN		4.4
Cr/CrN-2		5.6
Cr/CrN-4		7.1
Cr/CrN-8		7.7
Cr/CrN-32		6.6

Table 3

Sample	Max. applied load [N]	L_c [N]
Ti	30	8.5
TiN		16.4
TiTiN-2		23.3
TiTiN-4		16.1
TiTiN-8		13.6
TiTiN-16		21.8
TiTiN-32		22.9

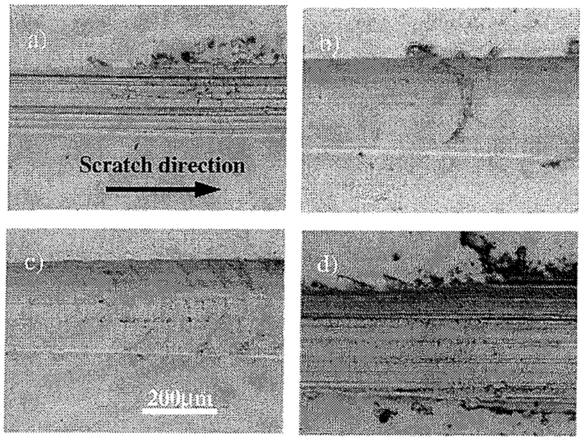

Fig. 8. Images of scratch path up to critical load L_c (a) Ti: single layer, (b) TiN single layer, (c) Ti/TiN 4 layers and (d) Ti/TiN 32 layers.

As expected, the titanium coating was softer and showed cracks formation much earlier than the chromium one. On the other hand, the TiN turned out to be more resistant to cracking than the CrN counterpart for single and multilayer coatings. In all cases, the Ti/TiN type coatings presented conformal type bucking cracks. The loads under which first cracks appeared were treated as the critical load L_c for the respective coating. Results of the scratch test of multilayer materials based on the Ti/TiN composition are presented in Table 3 and Fig. 8.

4. Discussion

The microstructure observations of the Cr/CrN and Ti/TiN multilayer coatings showed that the PLD gives very good control over the individual metal or nitride layer thickness down to at least 30 nm. The first metallic layer, serving as a buffer for the whole coating, was characterized by a very fine and heavily defected microstructure, while the next metallic layers showed coarser, less defected structures even as compared with the nitride layers. The reason for the different microstructure of the buffer layer might be related to the fact that its deposition serves as a final pumping stage of the vacuum system and therefore it either contains oxides or at least a higher level of oxygen as confirmed by EDS microanalysis. The presence of oxides usually increases material brittleness and compromises the coating adherence, so the target ablation should start with the substrate covered with a shutter or protected by other means. On the other hand, the coarser microstructure of the metallic interlayers is a positive sign indicating that they might be quite effective in their crack arresting role.

The scratch test experiments confirmed the very good resistance to cracking of the chromium layers and the rather poor resistance of CrN. The Cr/CrN multilayers showed a weak dependence of crack resistance to an increasing number of layers in the coatings, which stabilized at roughly 50% improvement over CrN. This however is still three times less than the reference chromium coating. The single layer titanium showed a medium resistance to cracking, i.e. approaching those of Cr/CrN multilayers, while the TiN was nearly two times better. The Ti/TiN multilayers, similar to TiN, presented a varying resistance to cracking with an increasing number of layers, but in this case the average resistance to cracking for the majority of coatings was significantly higher than the starting TiN. Comparing the results of the performed scratch test it is evident that sandwiching of monolayer TiN coatings with titanium interlayers might still improve their mechanical properties. However, the substitution of TiN by CrN or a Cr/CrN multilayer means a significant decrease of the coating wear properties at least at the present stage of the research.

The investigations indicate that both deposition of coatings built of a higher number of layers (i.e. thinner ones) should be possible and that, especially in case of Ti/TiN coatings, they might have an even better resistance to cracking.

5. Conclusions

1. The PLD technique allows to produce coatings consisting of well distinguishable layers with a thickness down to at least 30 nm.
2. The metallic buffer layers are characterized by the smaller columnar crystallite size and the highest defect density, what might rise their hardness but compromise their coating adhesion.
3. The intermediate metallic layers showed a larger and less defected columnar structure as compared with the nitride layers, what should improve the coating toughness.
4. Switching from single layer to multilayered metal/nitride coatings of the same thickness improved the resistance to scratch test comparing the Ti and TiN single layered with the Ti/TiN multilayer composition and the CrN single layer with the Cr/CrN multilayer, but decreased comparing to the Cr single layer with the Cr/CrN ones.

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