Mechanical properties dependence on the modulation period in multilayered TiN/ZrN coatings

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Abstract. This article presents results from a study on the properties of nanostructured multilayered TiN/ZrN coatings with different modulation periods deposited by cathodic-arc evaporation from Ti and Zr targets in nitrogen atmosphere on high-speed steel substrates. The thickness of the TiN-ZrN bilayers varied from 12 nm to 52 nm depending on the rotation speed of the holder. In order to investigate the effect of heat treatment on the mechanical and structural properties, the multilayer ZrN/TiN coatings were annealed in Ar atmosphere at different temperatures for two hours. The surface morphology, elemental composition, nano-hardness and adhesion strength of the as-deposited and annealed coatings were analyzed by scanning electron microscopy complemented with energy dispersive X-ray spectroscopy analysis, and nanoindentation and micro-scratch tests. The results obtained show that the mechanical properties of multilayer TiN/ZrN coatings are considerably improved in comparison to those of the monolayer ZrN and TiN coatings.

1. Introduction

Transition metal nitrides have attracted the attention of various research groups due to their extraordinary physical and chemical properties, such as: high melting point, high hardness, high wear resistance, corrosion resistance and good electrical conductivity. TiN and ZrN have been studied increasingly as hard coatings [1, 2]. In terms of applications, however, their poor oxidation resistance causes instability in their structure and properties at high temperatures. Further improvements of the nitride coatings have been sought, e.g., coatings based on the Ti-Zr-N system were deposited using a variety of deposition methods in order to improve the hardness and oxidation resistance [3, 4]. Recently, multilayered structures have attracted wide attention from both the scientific and the industrial communities because of their promising properties. These structures consist of alternating layers of two different materials with nanoscale dimensions deposited onto a substrate. Experimental studies have shown that multilayer coatings manufactured with transition metal nitrides have a hardness that exceeds that of the binary compounds that constitute them. This has been found in the multilayers VN/AlN, AlN/TiN [5, 6], NbN/TiN, MoN/TiN and TaN/TiN [7] grown by magnetron sputtering. These films have demonstrated improved hardness and thermal stability, and higher

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resistance to oxidation-and wear. Other multilayer coatings, such as TiN/ZrN and CrN/ZrN, were deposited by cathodic arc evaporation and the effects of the composition ratio and the modulation period on the mechanical properties were discussed [8-10].

In this work, TiN/ZrN multilayer coatings with different modulation periods were prepared by cathodic arc deposition and the relationship was studied between the bilayer thickness and the coatings’ mechanical properties.

2. Experimental details

2.1. Deposition of TiN/ZrN coatings
TiN, ZrN and TiN/ZrN multilayered coatings with different modulation periods were prepared using a cathodic arc deposition system equipped with two cylindrical Ti and Zr evaporators mounted oppositely. The current through the Ti cathode was 110 A and 120 A, through the Zr cathode. Before deposition, the substrates were cleaned by plasma using a DC bias voltage of –1000 V for 15 min. The coatings were deposited under identical deposition conditions: substrate heating 300 °C; substrate bias 80 V; nitrogen flow 460 sccm; substrate holder rotation speed 2, 3, 5 and 10 rpm; deposition time 53 min; base pressure in the vacuum chamber 4.0×10⁻³ Pa and working pressure 0.33 Pa.

Four series of experiments were performed for deposition of multilayered TiN/ZrN coatings with modulation periods of 12 nm, 20 nm, 32 nm and 52 nm. Monolayer TiN and ZrN were also prepared, for comparison. The multilayered coatings were deposited by alternately rotating the substrates between the plasmas of the Ti and Zr targets.

2.2. Study of coating properties
The mechanical properties were investigated using Compact Platform CPX (MHT/NHT) CSM Instruments equipment, which includes a nanoindentation module (NHT), a micro scratch module (MST) and an optical video microscope with a CCD camera, installed together on the same platform. The nanoindentation was performed by a triangular diamond Berkovich pyramid in the loading interval 10 – 500 mN. The nanohardness (H) and elastic modulus (E) were calculated from nanoindentation load-displacement data using the Oliver & Pharr method [11]. The adhesion strength of the coatings to the substrate material and the friction coefficient were evaluated using MST equipped with a spherical Rockwell indenter with a radius of 200 μm under the following test conditions: progressively increasing pressing force in the range 1 – 30 N; loading rate 1.0 N/min; acoustic emission detector sensitivity 9. The character of the resulting damages was assessed by observations with an optical video microscope equipped with a CCD camera.

The surface morphology observation and composition analysis were performed on a JEOL JSM 6390 electron microscope equipped with an INCA Oxford EDS energy dispersive detector. Surface images were also obtained in secondary electrons (morphology contrast) and back-scattered electrons (density contrast).

3. Results and discussion

3.1. Mechanical properties
3.1.1. Nanohardness. The mechanical parameters of the formed coatings were investigated in dependence on the modulation period (λ) in multilayered TiN/ZrN coatings. The nanohardness (H) and elastic modulus (E) were calculated from nanoindentation load-displacement data at a periodic loading and unloading of the samples. The indentation depth was limited to less than 10% of the film thickness (300 – 500 nm) to minimize the effect of the substrate on the measurements. As presented in table 1, all as-deposited multilayer coatings demonstrated a high hardness (28.5 – 32 GPa), excluding the coating with a 52-nm bilayer period. The results show that the mechanical properties of multilayer TiN/ZrN coatings were considerably improved in comparison to those of the monolayered ZrN and TiN coatings, which exhibited a hardness of about 23 GPa and 25 GPa, respectively. The study also
revealed a dependence of the mechanical properties on the bilayer period. The maximum hardness of 32 GPa was determined for the coating with a 12-nm bilayer period. This coating also exhibited a good elasticity of 375 GPa and a plastic deformation resistance of 0.23 GPa. However, the best adhesion properties and the lowest coefficient of friction were shown by the coating with a 20-nm bilayer period. The results obtained are in good agreement with the results discussed in [8, 12-14].

Table 1. Mechanical properties of TiN, ZrN and TiN/ZrN coatings.

| Samples       | Bilayer period \( \lambda \) [nm] | Thickness \( D \) [μm] | Hardness \( H \) [GPa] | Elastic modulus \( E \) [GPa] | Plastic deformation resistance \( H/E \) [Gpa] | Friction coefficient \( \mu \) |
|---------------|-----------------------------|---------------------|-------------------|-----------------------------|--------------------------------|---------------------|
| TiN           | -                           | 3.3                 | 25                | 466                         | 0.07                          | 0.14                 |
| ZrN           | -                           | 4.5                 | 23                | 374                         | 0.09                          | 0.12                 |
| TiN/ZrN       | 12                          | 5.4                 | 32                | 375                         | 0.23                          | 0.13                 |
| -             | 20                          | 5.0                 | 30                | 405                         | 0.17                          | 0.10                 |
| -             | 32                          | 4.9                 | 28.5              | 422                         | 0.13                          | 0.17                 |
| -             | 52                          | 6.0                 | 26                | 405                         | 0.11                          | 0.16                 |
| TiN, 700°C    | -                           | 3.3                 | 11                | 341                         | 0.01                          | 0.22                 |
| TiN/ZrN, 500°C | 12                          | 5.4                 | 30                | 356                         | 0.21                          | 0.10                 |
| TiN/ZrN, 700°C | 12                          | 5.4                 | 24                | 398                         | 0.09                          | 0.14                 |

Since the as-deposited coatings with \( \lambda = 12 \) nm demonstrated the highest values of the nanohardness and plastic deformation resistance, the further investigations were focused on them. The experimental results with the annealed coatings showed that increasing the treatment temperature to 700 °C causes a decrease of the coating hardness and a slight increase in the surface roughness and the friction coefficient. However, it should be pointed out that the hardness of the TiN/ZrN kept a high value (24 GPa) after annealing. We thus conclude that the thickness of the bilayer period plays a key role for the mechanical properties of the multilayered coatings [15-17].

3.1.1. Adhesion. During the tests, the load was increased progressively in a linear mode from 1 N to 30 N for scratch lengths of 1 mm and 3 mm and a constant scratch speed. The measuring device registered the penetration depth and the acoustic emission along the length of the track. Three scratches on the coated HSS substrates for each TiN/ZrN sample were conducted in order to determine the adhesion strength. The critical load \( (L_c) \) values were determined after the test by optical microscopy observation of the damages formed in the scratch tracks and from the recorded acoustic emission (AE) and friction force \( (F_i) \) signals. The critical loads \( L_{c1} \) and \( L_{c2} \) indicate the appearance of the first cohesive and adhesive cracks, respectively [14, 18].

The test consisted in applying a continuously increasing load on the system coating-substrate at a constant speed. The scratching point causes an increase of the elastic and plastic deformation until damage occurs in the surface region. Figure 1(a, b, c) shows scratch graphs of the TiN/ZrN_ml coating with a 12-nm bilayer period before and after annealing. It was seen that increasing the scratch length and the normal load changes the values of the friction force and the acoustic emission.

The as-deposited multilayer TiN/ZrN coatings with \( \lambda = 12 \) nm showed a very good adhesion (figure 1a) within the loading range 1 – 30 N. The friction coefficient was estimated at \( \mu = 0.13 \) against a diamond indenter at a maximum friction force of \( F_i = 3.8 \) N. After annealing at 500 °C, the coatings demonstrated excellent adhesion (figure 1b) without chipping and spallation. \( F_i \) and \( \mu \) decreased to 2.9 N and 0.1, respectively. After annealing at 700 °C, no failures along the scratch track were observed (figure 1c). However, slightly pronounced brittle tensile cracks were observed. This was accompanied by a distortion of the friction force line and a rise in the acoustic emission signal at a loading of about 26 N. In this case, an increase in \( F_i \) and \( \mu \) to 4.23 N and 0.14, respectively, was established.
Figure 1. Scratch graphs of the TiN/ZrN multilayer coatings before and after annealing: a) as-deposited state; b) after annealing at 500 °C; c) after annealing at 700 °C. F_n – loading; AE – acoustic emission; F_t – friction force; µ – friction coefficient.

3.2. Surface morphology and composition
Figure 2(a,b,c) illustrates the SEM surface morphologies of TiN/ZrN coatings before and after annealing. A rather smooth surface was found for all as-deposited coatings. Generally, droplets can

Figure 2. High magnification SEM surface topography of a multilayer TiN/ZrN coating with 12-nm bilayers period before and after annealing: a) as-deposited state; b) after annealing at 500 °C; c) after annealing at 700 °C.
hardly be avoided during the deposition of coatings using the vacuum cathodic arc technique. The presence of micro-droplets on the surface (figure 2a) is clearly visible on the image. The same surface topography is observed for the TiN and ZrN coatings.

The elemental composition of a TiN/ZrN multilayered coating before and after annealing is presented in table 2. The EDS analysis revealed changes in the elemental composition after the annealing. Penetration of oxygen in the near-surface layer forms titanium and zirconium oxides on the coating surface due to substitution of nitrogen atoms by oxygen ones [19].

Table 2. Elemental composition of a TiN/ZrN multilayered coating with a 12-nm bilayer period before and after annealing obtained using EDS analysis.

| Element | Atomic % | as-deposited | annealed 500 °C | annealed 700 °C |
|---------|----------|--------------|-----------------|-----------------|
| Zr      | 28.0     | 16.52        | 17.92           |
| Ti      | 27.5     | 16.57        | 15.77           |
| N       | 44.5     | 28.12        | 9.93            |
| O       | -        | 18.62        | 45.16           |
| C       | -        | 20.17        | 11.22           |
| Total   | 100.0    | 100.00       | 100.00          |

4. Conclusions

A series of samples were prepared by varying the thickness of the alternating layers of TiN and ZrN, which defined the compositional modulation wavelength $\lambda$. All as-deposited multilayered TiN/ZrN coatings demonstrated a high hardness of 27 – 32 GPa, a very good adhesion to the substrates in the loading interval 1 – 30 N and a low friction coefficient ($\mu = 0.1 – 0.17$) against a diamond indenter. The maximum hardness, elastic modules and plastic deformation resistance values around 32 GPa, 375 GPa and 0.23 GPa, respectively, were determined for the coating with a 12-nm bilayer period. However, the best adhesion properties and the lowest coefficient of friction ($\mu = 0.1$) were demonstrated by the coating with a 20-nm bilayer period. The optimum annealing temperature for the investigated coatings in view of their hardness and adhesion strength was found to be 500 °C. Increasing the treatment temperature to 700 °C caused oxidation of the coatings, a decrease in the coating hardness, and a slight rise in the surface roughness and the friction coefficient. The results can be explained by the influence of the dimensional factor of interphase boundaries, which is greatly enhanced in a multilayered system with a nanometer-scale thickness of the bilayers.

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