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Preparation and tribologic properties of Ti and Zr nitride multilayer coatings

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This paper focuses on synthesis and characterization of Zr/Ti and Ti/Zr nitride multilayer coatings by magnetron plasma sputtering to enhance the tribologic properties. The synthesis of nitrides was achieved by non-reactive deposition using Ti or Zr nitride targets or by reactive deposition using Ti or Zr targets in the presence of nitrogen. The formation of nitride layers was highlighted by XRD, EDX and XPS investigations, while the tribologic properties were made with HFRR equipment. The tribological study showed that the coefficient of friction and wear scar diameter decrease in multilayer films with zirconium nitride as the upper layer.

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Keywords: TiZr coating, ZrTi coating, Reactive deposition, Tribologic properties, Plasma sputtering

1. Introduction

The surface of a material is often the first point of contact with its environment, and it is therefore subject to a wide range of external factors, such as temperature, humidity, corrosion, and wear [1-3]. These factors can cause degradation, leading to reduced performance and even failure.

There are several possibilities for protecting a surface, respectively, by acting on the environment with which it comes into contact (by using fluids capable of protecting against corrosion or additive lubricants to reduce wear) or by modifying the surface, by depositing functional layers or coatings [4-6]. Surface engineering is an essential tool for mitigating these effects by modifying the surface of a material to improve its resistance to external influences. Surface engineering is the process of modifying the surface properties of a material to achieve desired performance characteristics. The significance of surface engineering in modern industry cannot be underestimated. It plays a critical role in the performance, reliability, and the lifespan of a wide range of products, from medical implants and electronics to aircraft components and automotive parts [7-8].

There are several common surface engineering techniques that are used to modify the surface properties of materials. These include coating, surface functionalization, ion implantation, surface patterning, surface roughening, surface modification by laser, surface grafting, surface oxidation, surface alloying, and surface doping.

Sputtering is a common technique for physical vapor deposition (PVD), one of the methods of producing thin film coatings. Sputtering uses a target of a pure material and an inert gas, usually argon. If the material is a single pure chemical element, the atoms are sputtered from the target to the substrate.

However, it is possible to use a reactive gas such as oxygen or nitrogen with or without the inert gas. When this is done, the non-inert ionized gas can chemically react with the vapor cloud of the target material and produce a molecular compound that then becomes the deposited film. There are already a few decades since nitrides or carbonitrides of titanium or zirconium become attractive for many applications due to their superior mechanical strength, chemical stability, corrosion resistance, biocompatibility [7, 9-11]. Both titanium and zirconium layers or nitrides of these elements have exhibited outstanding properties, initially in medical applications, later in various applications, as well as tribological ones. However, multiple layer deposits were very little

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investigated, therefore, in this paper were investigated the features of multiple layers of zirconium and titanium nitrides on adhesion and tribologic properties.

2. Experimental part

2.1. Materials

Titanium, zirconium targets used for reactive sputtering deposition, titanium nitride and zirconium nitride targets used for non-reactive deposition were 99.5% purity and were purchased from the Kurt J. Lesker Company. Disks used as substrate for deposition of coatings are made of stainless-steel AISI-E 52100/535A99 (with 10 mm diameter, roughness of Ra=0.020 µm and a hardness of RC 76-79). Argon has purity 4.8 and nitrogen 5.6 and were supplied from Linde Gas. Acetone and isopropyl alcohol were provided by Merck.

2.2. Experimental method

TiN/ZrN or ZrN/TiN multilayer coatings were prepared by magnetron sputtering in the presence of Ar for non-reactive tests by using TiN and ZrN targets, while TiN/ZrN or ZrN/TiN multilayer coatings were prepared by magnetron sputtering in the presence of Ar and N_2 for reactive tests by using Ti and Zr targets.

For deposition of multilayer coatings, it was used a magnetron that had holders for two targets. Before each experiment, the magnetron was cleaned with acetone and isopropanol to remove any traces of dust or previous deposits. Experiments were performed with titanium/titanium nitride and zirconium/zirconium nitride targets measuring 2" diameter and 0.125" thick, +/-0.010". The distance between the target and the substrate was 75 mm. The working pressure was $5.2x10^{-3}$ mbar and the base pressure $2.3x10^{-5}$ mbar. The angle corresponding to the magnetron gun was set to 19^{o}. Radio frequency power was 100 Watt. The Ar flow was fixed at 50 sccm, while the N_2 flow was 7 sccm for the reactive deposition. The deposition time depended on the deposition method and the nitride type. The tests showed that the deposition speed for TiN would be 5.8 nm per minute and for ZrN 10 nm/minute in a non-reactive system, and for the samples deposited in the reactive system, the deposition rate was 2.5 nm/min for Ti and 2 nm/min for Zr. Both targets (Ti and Zr or TiN and ZrN) have been mounted in the magnetron, which means that the "dead" time of the magnetron is reduced because as soon as the deposition of the first layer is finished, the deposition of the second layer begins. The label of the multilayer coatings were made so that the first nitride represents the first layer deposited on the stainless steel disc while the second nitride is the upper layer.

The XRD investigation was carried out with Bruker Discovery equipment, Germany equipped with a copper anode (CuKα1=1,54056 Å).

SEM-EDX investigations were carried out using the equipment model FEI S Inspect, USA, working at 20 kV.
XPS investigations for surface chemistry analysis, were carried out on K-Alpha, by Thermo Fisher Scientific, US, performed with a monochromatic (Al Kα) X-ray beam, on a 300×300 µm spot area in a spectrometer equipped with a flood gun for charge compensation.

Tribological investigations were conducted on HFRR equipment provided by PCS Instruments, UK.

3. Results and discussions

3.1. EDX investigations

The deposition rate of the layers was controlled to obtain thicknesses of each layer of 100 nm, while the total thickness of the multilayer is 200 nm. To confirm the formation of the ZrN and TiN substrate deposited in a non-reactive but also reactive system, EDX analyzes were performed in different areas of the substrate surface. The corresponding peaks can be seen in figure 1.

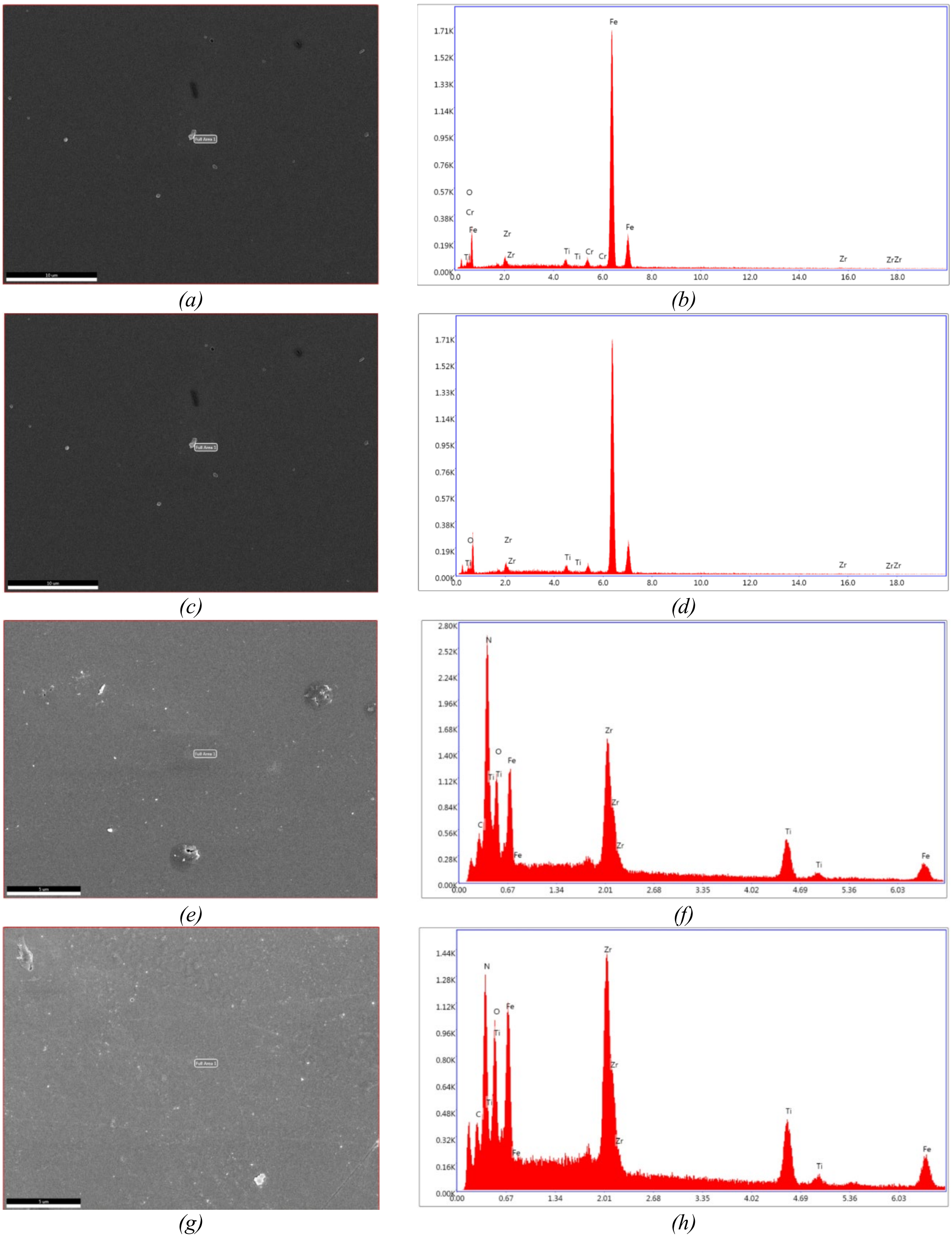

Fig. 1. EDX spectroscopy of (a) ZrN/TiN non-reactive, analysis area (b) ZrN/TiN non-reactive corresponding peaks (c) TiN/ZrN non-reactive, analysis area (d) TiN/ZrN non-reactive corresponding peaks, (e) ZrN/TiN reactive, analysis area (f) ZrN/TiN reactive corresponding peaks (g) TiN/ ZrN reactive, analysis area (h) TiN/ ZrN reactive corresponding peaks.

The details corresponding to the EDX spectra for Zr and Ti samples in non-reactive and reactive systems are presented in table 1.

Table 1. EDX results.

Element	Ti	Cr	Fe	O	Zr	N_2
Sample	Atomic %					
ZrN/TiN non-reactive	8.28	2.16	61.99	24.16	3.41	-
TiN/ZrN non-reactive	2.05	-	6.23	79.87	11.85	-
ZrN/TiN reactive	24.69	1.95	6.51	14.36	11.43	41.06
TiN/ZrN reactive	20.98	1.99	8.72	17.96	15.53	34.82

Higher atomic percentage of Zr was recorded for the samples with ZrN as the upper layer, while higher atomic percentage of Ti was recorded for the samples with TiN as the superior layer. Spectra corresponding to layers obtained by reactive sputtering deposition, presents high atomic percentage of N_2 due to its use as inert gas together with Ar in the deposition chamber. In general, it is observed that for depositions in a reactive system, the percentage of oxygen decreases compared to samples deposited in a non-reactive system. Fe and Cr from the spectra are related to the chemical composition of the stainless steel discs used as supports.

3.2. XRD investigations

The results of X-ray diffraction (XRD) analysis performed on the TiN/ZrN and ZrN/TiN films obtained by non-reactive method are presented in figures 2-3. The pattern from figure 2 presents several peaks with intensity ($2\Theta = 44^o$), which belong to ZrO_2 (102), being specific to the monoclinic phase of zirconium. The peaks corresponding to $2\Theta=64^o$ indicate the presence of ZrN (311), and those at $2\Theta=62^o$ indicate the presence of ZrN (222).

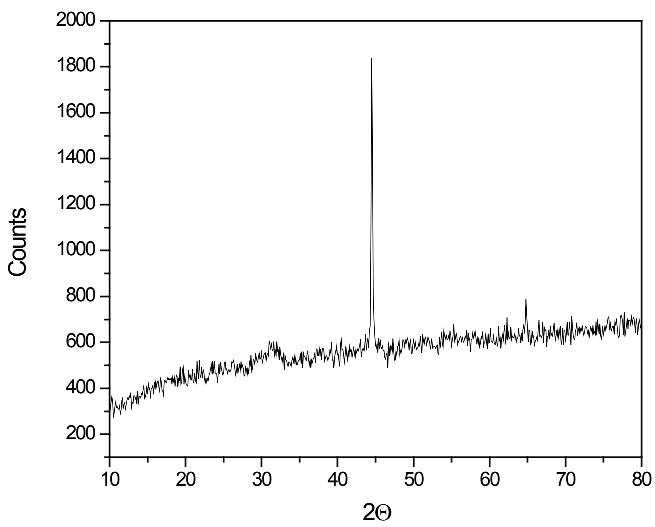

Fig. 2. XRD diffraction of TiN/ZrN non-reactive.

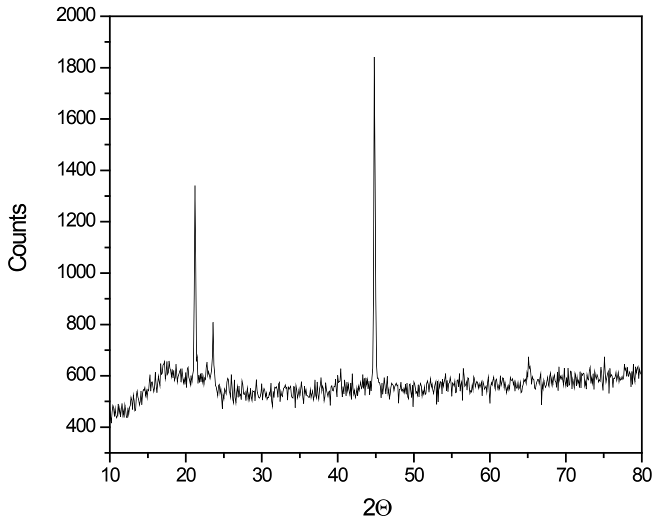

Fig. 3. XRD diffraction of ZrN/TiN non-reactive.

The diffractogram from fig. 3 shows that for the sample of ZrN/TiN there are peaks of high intensity at 2θ=21°, 24° and 44°. The peaks recorded at 21 and 24° correspond to ZrO_2 (110), at 44° to TiN (200) and the small peak at 65° correspond to TiO_2.

3.3. XPS spectroscopy

The high resolution XPS spectra of the ZrN/TiN and TiN/ZrN multilayers coatings synthesized via non-reactive or reactive methods are given in fig. 2.

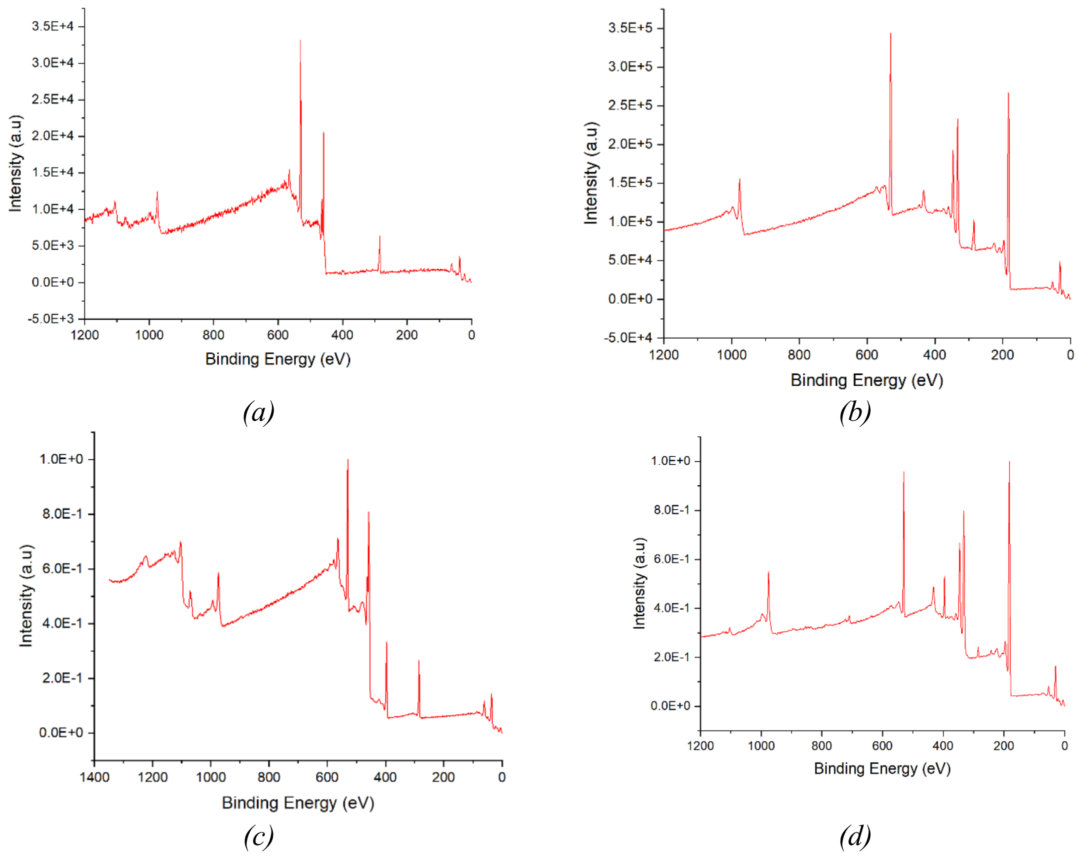

Fig. 2. XPS spectroscopy of (a) ZrN/TiN non-reactive (b) TiN/ZrN non-reactive (c) ZrN/TiN reactive, (d) TiN/ ZrN reactive.

Table 2. Chemical composition of the surface region of coatings in relative atomic percent (at.%).

Spectra	Samples			
	ZrN/TiN non-reactive	TiN/ZrN non-reactive	ZrN/TiN reactive	TiN/ ZrN reactive
Zr3d	-	21.78	-	13.72
Ti2p	23.0	-	25.3	-
O1s	49.06	55.98	29.17	21.84
C1s	27.94	22.24	20.61	4.79

All XPS spectra have peaks at 284.8 eV binding energy related to the aliphatic C1s.

Samples with zirconium nitride top layer (b and d) show Zr 3d spectra at around 182 eV and 186 eV binding energy, while the samples with titanium nitride top layer (a and c) show $Ti2p_{3/2}$ spectra at around 454 eV corresponding to Ti metal, at $Ti2p_{1/2}$ 458 eV correlated to TiO_2 and 464 eV for TiN [12-14]. The N1s peak is composed of two components at 397.2 and 399 eV in binding energy are related to N-Metal and N-O.

3.4. Tribological investigations

The tribological investigations were carried out on the HFRR equipment with which the wear scare imprinted on the steel ball that is rubbed on the disc on which the functional layers were deposited was evaluated.

The equipment used is a class 1 type tribosystem ball on the disc. The test involves the friction of a steel ball AISI-E 52100 / 535A99 (with a roughness of Ra = 0,050 μm and a hardness of RC 58-66) on a steel disc AISI-E 52100 / 535A99 (with a diameter of 10 mm, with a diameter of, a roughness of Ra = 0,020 μm and a hardness of RC 76-79) in the presence of 2 ml of lubricant.

In our investigations, the steel disc was subjected to magnetron sputtering deposition.The lubricant selected for wear tests is a SAE 20 mineral base oil with good lubricating properties therefore the tribological characteristics are not affected by the quality of the lubricant.

The physical chemical properties of SAE 20 are published in our previous paper [15]. The results of tribologic investigation are presented in table 3.

Table 3. Result of tribologic investigations.

Sample	Wear scar diameter, μm	Coefficient of friction
ZrN/TiN non-reactive	135	0.085
TiN/ZrN non-reactive	130	0.081
ZrN/TiN reactive	146	0.063
TiN/ZrN reactive	127	0.054

Tribological investigations have shown that multilayers deposited in the reactive system seem to be more efficient from tribological point of view because both the wear scar diameter and the coefficient of friction recorded are lower than those corresponding to the multilayer deposited in non-reactive system. Also, the results are better for the samples for which the zirconium nitride layer is on top and therefore in direct contact with the ball of the friction coupler, meaning that Zr is more wear-resistant than Ti.

4. Conclusions

X ray diffraction investigations coupled with EDX and XPS have demonstrated the formation of titanium and zirconium nitride multilayers. In recent years, functional layers have demonstrated their efficiency in the most diverse fields, from the medical field to surface engineering to their protection. Most of the studies refer to applications of monolayer layers of titanium, zirconium, titanium nitride or zirconium nitride and very few studies consider multilayers and their use in tribological applications. The tribological investigation has shown that tribological properties are more impacted by multilayer deposits than monolayer nitride layers. The use of multipliers resulted in an improvement in tribological properties compared to those obtained in monolayers. probably due to the fact that adhesion increases in the surface and when zirconium nitride is the upper layer, the coefficient of friction and the diameter of the wear stain are smaller than when titanium nitride is the top layer.

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