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JOURNAL OF THE BALKAN TRIBOLOGICAL ASSOCIATION™

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Journal of the Balkan Tribological Association is an International Journal edited by the Balkan Tribological Association for rapid scientific and other information, covering all aspects of the processes included in overall tribology, tribomechanics, tribochemistry and tribology.
The Journal is referring in Chem. Abstr. and RJCH (Russia).

Aims and Scope

The decision for editing and printing of the current journal was taken on Balkantrib'93, Sofia, October, 1993 during the Round Table discussion of the representatives of the Balkan countries: Bulgaria, Greece, Former Yugoslavian Republic of Macedonia, Romania, Turkey and Yugoslavia. The Journal of the Balkan Tribological Association is dedicated to the fundamental and technological research of the third principle in nature – the contacts. The journal will act as international focus for contacts between the specialists working in fundamental and practical areas of tribology.

The main topics and examples of the scientific areas of interest to the Journal are:

(a) overall tribology, fundamentals of friction and wear, interdisciplinary aspects of tribology;
(b) tribotechnics and tribomechanics; friction, abrasive wear, adhesion, cavitation, corrosion, computer simulation, design and calculation of tribosystems, vibration phenomena, mechanical contacts in gaseous, liquid and solid phase, technological tribological processes, coating tribology, nano- and microtribology;
(c) tribochemistry – defects in solid bodies, tribochemical emissions, triboluminescence, tribochemiluminescence, technological tribochemistry; composite materials, polymeric materials in mechanics and tribology; special materials in military and space technologies, kinetics, thermodynamics and mechanism of tribochemical processes;
(d) sealing tribology;
(e) biotribology – biological tribology, tribophysiotherapy, tribological wear, biological tribotechnology, etc.;
(f) lubrication – solid, semi-liquid lubricants, additives for oils and lubricants, surface phenomena, wear in the presence of lubricants; lubricity of fuels; boundary lubrication;
(g) ecological tribology; the role of tribology in the sustainable development of technology; tribology of manufacturing processes; of machine elements; in transportation engineering;
(h) management and organisation of the production; machinery breakdown; oil monitoring;
(i) European legislation in the field of tribotechnics and lubricating oils; tribotesting and tribosystem monitoring;
(j) educational problems in tribology, lubricating oils, fuels and contacts;
(k) contacts – mechanical, agricultural, chemical, medical, social environments.

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COMPARATIVE STUDY OF WEAR RESISTANCE OF TiO_2 COATINGS WITH CERIUM AND CHROMIUM ADDITIVES

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ABSTRACT

The spray pyrolysis method has been applied to obtain cerium and chromium modified titania coatings. Wear resistance tests of the obtained samples have been carried out to compare the effects of Ce and Cr additives. The experimental runs of abrasive wearing of coatings were realised by means of the test rig TABER ABRASER according to the kinematical scheme 'disk-on-disk'. The absolute wear resistance was measured by mass *I* in m/mg. The XRD patterns identified nanosised anatase phase. The oxidation states of Ti, Cr and Ce were characterised by XPS study. The AFM images have revealed that in the modified coatings the films particles have strong adhesion to the substrate, while on the reference sample of non-modified TiO_2 coatings there are spots, which have been completely damaged. After 400 abrasive cycles the surface roughness of the Cr-doped sample was decreased 5.7 times. The increase in cerium and chromium concentration was established to result in enhancement of wear resistance, compared to the non-modified TiO_2 coating. The performance of the 10% Cr-containing coating was superior to that of the Ce-containing coatings.

Keywords: tribological properties, TiO_2 films, Cr- or Ce-modified TiO_2 films, wear behaviour, surface topography.

* For correspondence.

AIMS AND BACKGROUND

Over the past years industrial trends have required better and better wear resistant coatings. Abrasive wear resistance is a subject of great importance in mining, mineral processing, agriculture, etc. because more than 50% of wear-related failures of industrial equipment are caused by abrasive wearing off. Nanotribology deals with the preparation and investigation of the materials with specific physicochemical and mechanical properties, which provide optimum regime of friction and wearing off. Ceramic coatings possess good resistance to corrosion, heat and wear than metals[1,2]. Among them TiO_2 coatings have attracted much attention due to their good wear and corrosion resistance, biocompatibility and low price. In Refs 3 and 4 Zhang et al. investigated the tribological properties of TiO_2 coatings, obtained by sol gel technology. To the best of our knowledge there are no data in the available literature about the preparation of TiO_2 sprayed coatings, exhibiting good wear resistance. Recently, we reported about preparation of sprayed TiO_2 coatings on aluminum substrate, which have promising tribological properties[5]. In this study we present the effects of cerium and chromium additives on the surface topography, microstructure and wear resistance of sprayed titania coatings.

EXPERIMENTAL

Aluminium foil sheets were used as substrates. Titanium chloride, dissolved in isopropanol, was used as titanium precursor solution. For the preparation of Ce or Cr modified TiO_2 coatings, $Ce(NO_3)_3.6H_2O$ or $Cr(NO_3)_3.9H_2O$ solutions were mixed with the corresponding quantity of titanium chloride solution. The concentrations of additives in the so obtained solutions were varied within in the range between 2 and 30 at.% with respect to the Ti content. The phase and chemical composition of the samples have been studied by XRD, XPS and AFM analyses. The mean crystallite sizes of the samples have been estimated using the Scherrer formula.

The phase composition of the samples was studied by X-ray diffraction (XRD) with CuK_α-radiation (Philips PW 1050). The crystallite size was estimated based on XRD patterns. The surface analyses of the titania coatings were carried out by X-ray photoelectron spectroscopy (XPS). The measurements were performed in VG ESCALAB II electron spectrometer using AlK_α radiation with energy of 1486.6 eV. The binding energies were determined with an accuracy of ±0.1 eV. The chemical composition of the films was investigated on the basis of areas and binding energies of O1*s* and Ti2*p* photoelectron peaks (after linear subtraction of the background and Scofield photoionisation cross-sections). The surface topography was studied by means of atomic Force microscope (AFM) (NanoScopeV system, Bruker Inc.) operating in tapping mode in air at room temperature. The silicon cantilevers (Tap 300 Al-G, Budget Sensors, Innovative solutions Ltd, Bulgaria) were used with 30 nm thick aluminum reflex coating. The reported by the producer cantilever spring constant was in the range of 1.5–15 N/m, the resonance frequency was 150 ± 75 kHz and the tip radius was less than 10 nm. The scan rate was set at 1 Hz and the images were captured in the height mode with 512×512 pixels in a JPEG format. Subsequently, all the images were flattened by means of the Nanoscope software.

The obtained samples were subjected to wear resistance tests. The experimental runs of abrasive wearing resistance of the coatings were realised by means of the test rig TABER ABRASER according to the kinematical scheme 'disk-on-disk'[6,7].

The device used for this test is shown in Fig. 1. Specimen (1) is mounted on a horizontal bearing plate (2) which is driven by an electric motor at a constant angular velocity (5) of 60 rpm. Abrasive roller (antibody) (3) made of plastic abrasive material CS 10, is mounted on a horizontal axis in the device. Thus the specimen (1) and the roller (3) are located in two orthogonal directions and at a constant angular velocity (5) of the specimen (1) and permanent normal loading, the friction in the contact area maintains a constant speed of rotation of the roller (3). The contact normal loading is transmitted by weights (6) through the axis of the roll; in this case there is one weight with a mass of 1.250 kg.

The procedure of the experimental study on abrasive wearing off is realised in the following sequence of operation steps:

– Cleaning of lubricants and drying of the identical specimens. The specimens represent disks of diameter 100 mm and thickness of 3 mm of the deposited coatings;

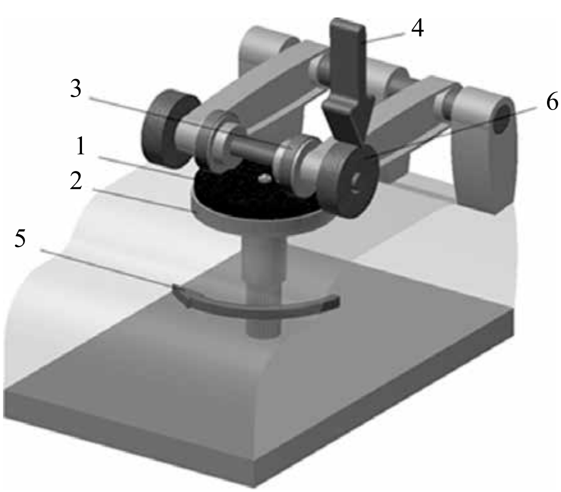


Fig. 1. 3D model of the apparatus for abrasive friction under dry wear conditions

– Measuring of roughness of the contact surfaces of the specimens before and after the wear test;

– Measuring of specimens mass m_o before and its mass m_i after a given friction path L by electronic balance WPS 180/C/2 of accuracy 0.1 mg. Before every measurement the specimens are cleaned with appropriate solution against static electricity;

– The specimen 1 is fixed on the carrying horizontal disk 3; then the normal load P is set. The friction path L is determined by the number of cycles read by the revolution counter 8.

Abrasive wearing off for all coatings is obtained by fixed identical operating conditions – nominal contact pressure given with the normal load P, average sliding speed V and parameters of the abrasive surface.

Table 1. Parameters of wear resistance experiments

Apparent contact area	$A_a = 0.26$ cm^2
Normal contact pressure	$P_a = 17.3$ N/cm^2
Average sliding speed	$V = 17.9$ cm/s

The experiment data are listed in Table 1.

The following parameters of mass wearing off are studied:

– Absolute mass m worn off;

– Average rate of mass dm/dt, mg/min wearing off;

– Absolute intensity of mass wearing off i, mg/m:

$$i = m/S \tag{1}$$

– The friction distance S is calculated by the corresponding number of cycles N and the distance R between the axis of rotation and the mass centre of the nominal contact site by the formulae:

$$S = 2\pi RN \tag{2}$$

– Absolute wear resistance by mass I, m/mg:

$$I = 1/i = S/m. \tag{3}$$

RESULTS AND DISCUSSION

The X-ray diffraction analyses of all samples revealed pure anatase crystallographic phase, presented by (101) peak (Figs 2 and 3). It has to be noted that the sample modified with 30 at.% of Cr is amorphous, while the XRD pattern of the respective 30Ce sample is registering strong amorphisation of the anatase phase. The solution compositions and crystallites size before and after abrasive tests of all samples are represented in Table 2. The modifying of TiO_2 by cerium or chromium leads to a slight increase in the size of the crystallites in the nanometer range before and after wear resistance tests (Fig. 2, Table 2). It has to be noted that

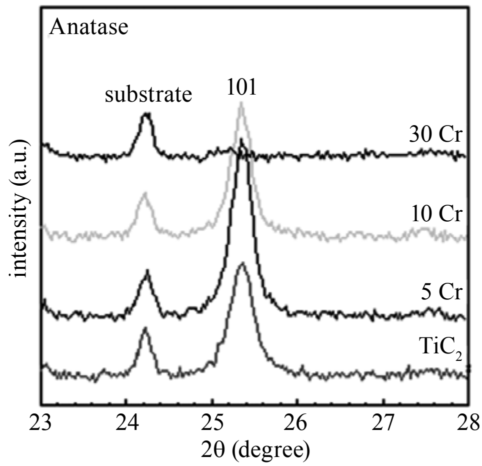


Fig. 2. XRD patterns of non-modified and chromium doped TiO_2 coatings

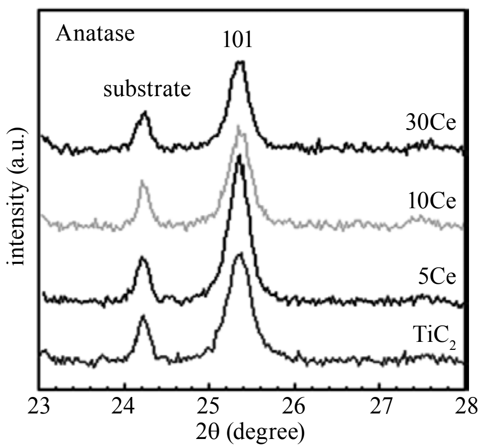


Fig. 3. XRD patterns of non-modified and cerium doped TiO_2 coatings

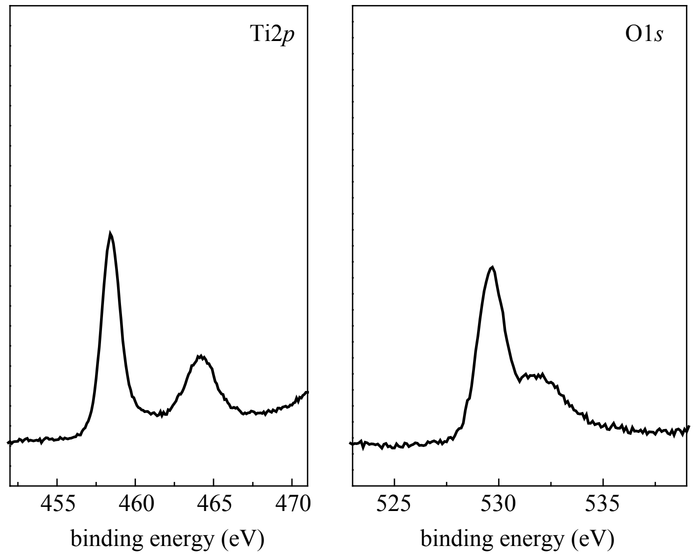
Table 2. Sample compositions and crystallite sizes

Sample code	Solution composition	Crystallite sizes before tests (nm)	Crystallite sizes after tests (nm)
TiO_2	$TiCl_4$	26	23
2Ce	$TiCl_4$+Ce (2 at.%)	–	–
5Ce	$TiCl_4$+Ce (5 at.%)	30	28
10Ce	$TiCl_4$+Ce (10 at.%)	27	27
15Ce	$TiCl_4$+Ce (15 at.%)	–	–
30Ce	$TiCl_4$+Ce (30 at.%)	31	28
2Cr	$TiCl_4$+Cr (2 at.%)	–	–
5Cr	$TiCl_4$+Cr (5 at.%)	29	29
10Cr	$TiCl_4$+Cr (10 at.%)	29	26
15Cr	$TiCl_4$+Cr (15 at.%)	–	–
30Cr	$TiCl_4$+Cr (30 at.%)	amorphous	amorphous

the anatase phase is preserved after 400 cycles of friction. After abrasive tests the crystallite sizes of all samples are only slightly lowered with about 1–3 nm.

The XPS analyses were applied for the surface observations of the samples. Figure 4 shows the Ti 2*p* core level spectra of the TiO_2 films, prepared from the solution of 10% Cr. The shape and the position of the $Ti2p^{3/2}$ peak at 458.5 eV indicate the presence of Ti^{4+} oxidation state. The O1*s* spectra (Fig. 4*b*) show a main peak at 529.7 eV and a small shoulder at 531.9 eV. The peak at 529.7 eV is assigned to oxygen bound to tetravalent Ti ions. The shoulder at 531.9 eV is ascribed to oxygen atoms in hydroxyl groups. The binding energy of the Cr 2*p* peak is 576.7 eV which is attributed to Cr_2O_3.

Fig. 4. Ti 2*p* and O 1*s* core level spectrum of the surface of 10Cr coating



The surface morphology of the TiO_2 coatings before and after 400 abrasive cycles was investigated by Atomic Force Microscopy (AFM). Typical topographical images of the surface of non-modified TiO_2 coatings before and after 400 abrasive cycles are shown at Figs 5*a* and 5*b*, respectively. The AFM images are presented in 2D and 3D format and they are also accompanied by sections across the sample surface. In the same manner, topographical images of the chromium modified TiO_2 coatings before and after 400 abrasive cycles are shown in Fig. 5*c* and Fig. 5*d*, respectively. The comparison of the AFM images of non-modified and modified TiO_2 coatings clearly demonstrates that after 400 abrasive cycles the coating surface becomes considerably smoother. The performed degree of roughness analysis shows a profound difference in the surface structure of the samples before and after the abrasive cycles test. It gives for the non-modified sample the mean roughness R_a, values of about 41 nm, while after performing the test this value drops down 6.8 times to about 6 nm. For the modified samples the calculated values for the surface degree of roughness R_a is about 52 nm before and 9 nm after the test. It means that after 400 abrasive cycles the surface roughness of the doped sample is decreased 5.7 times. The AFM images in Fig. 5 also reveal that in the modified coatings the films particles have strong adhesion to the substrate, while the reference sample of non-modified TiO_2 has spots, which have been completely erased and the coating is almost missing. After the abrasive tests the coatings roughness significantly lowers due to plastic deformation, as it is evidenced by the AFM images and the roughness analysis. This explanation is in accordance with the observations for TiO_2 sol gel coatings on glass substrate by Zhang et al.[3] The authors stated that such signs of plastic deformation indicate that

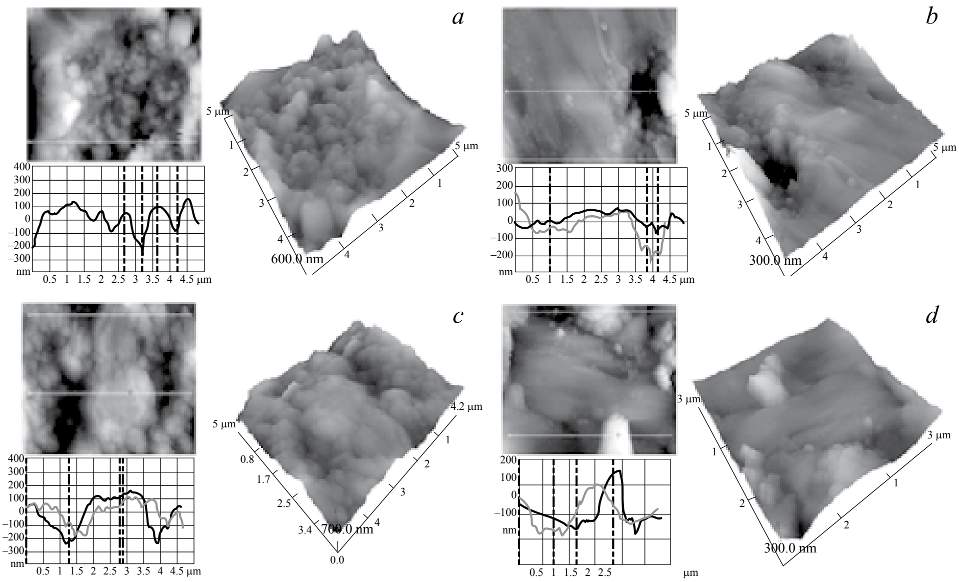


Fig. 5. AFM topographical images presented in 2D and 3D format, together with the spots on the sample surface of: non-modified TiO_2 coating before (*a*) and after 400 abrasive cycles (*b*), 10Cr coating before (*c*) and after 400 abrasive cycles (*d*)

the TiO_2 film has very good toughness or even super plasticity, which is consistent with the plastic deformation behaviour.

The modified TiO_2 coatings increase the wear resistance of the aluminum substrate. Both cerium and chromium concentration increases were found out to result in enhancement of wear resistance (Figs 6 and 7).

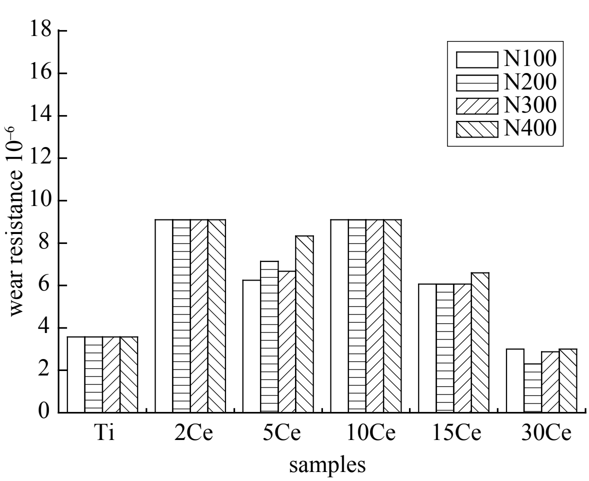
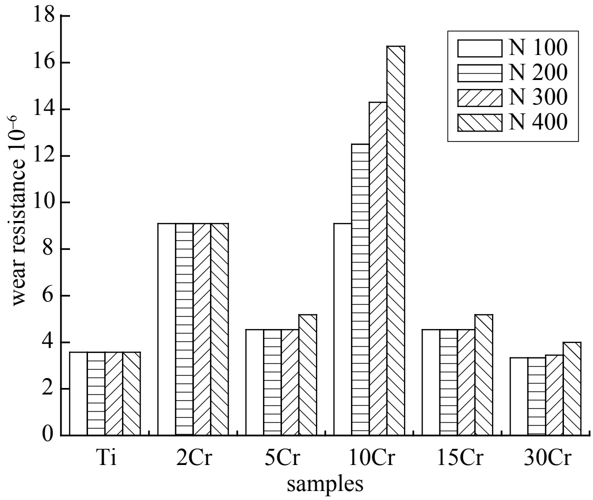


Fig. 6. Wear resistances of Ce modified TiO_2 samples after 100, 200, 300 and 400 abrasive cycles

Fig. 7. Wear resistances of Cr modified TiO_2 samples after 100, 200, 300 and 400 abrasive cycles



The increased concentration of the Ce additive does not promote significantly the wear resistance of the samples in comparison to the reference TiO_2 sample. Whereupon within the interval from 2 to 15 at.% no well expressed maximum is observed in this value (Fig. 6). The chromium modifier effect is expressed more strongly on the tribological properties of the layers. The titanium dioxide coatings modified with 10% Cr have the highest wear resistance (Fig. 7).

The increase in the content of the modifying agent chromium up to 10 at.% promotes considerably the wear resistance of the coatings, while for the 15Cr and 30Cr samples the wear resistance of the samples is decreased drastically. The improved wear resistance of modified TiO_2 coatings probably can be attributed to higher degree of crystallinity and good adhesion with the substrate, as it is evidenced by the AFM images. The AFM analyses revealed also that after the abrasive cycles the surface of the samples became considerably smoother with visible signs of plastic deformations.

CONCLUSIONS

Cerium and chromium modified titania coatings have been deposited on aluminum substrate by spray pyrolysis method. Some positive influence of the additives on the wear resistance of TiO_2 coatings has been established. The XRD study identified anatase crystallographic phase with nanosized crystallites in all samples, which shows tendency of amorphisation with the increasing of concentration of the modifiers. The non-modified sample has mean degree of roughness of $R_a = 41$ nm, while after the wear tests this value drops down about 7 times. For the modified samples after abrasive cycles the surface roughness is decreased 5.7 times, which is the result of plastic deformation. It was shown using AFM analyses that after wear tests the particles of modified coatings have strong adhesion to the substrate, while in the reference sample of non-modified TiO_2 there appear spots, which are completely erased and the coating is almost missing in some places. The modification of TiO_2 coatings with Ce or Cr up to 10 at.% increases significantly the wear resistance in comparison with the reference sample. The best tribological properties are exhibited by TiO_2 samples, modified with 10 at.% chromium.

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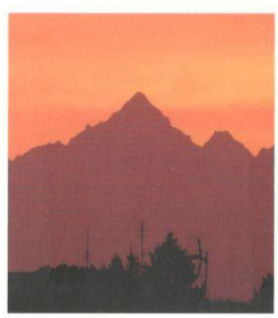
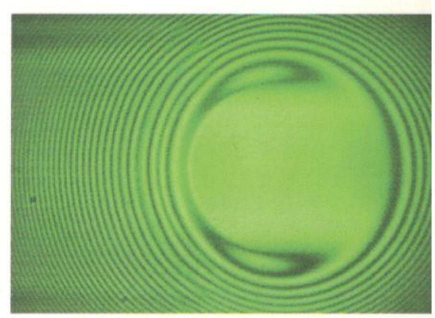

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1190 **Influence of Deposition Parameters of TiO2 Sprayed Films on the Abrasive Wear Resistance**
Mara Kandeva, *Technical University-Sofia, Sofia, Bulgaria*, Vladimir Blaskov, Irina Stambolova, *Bulgarian Academy of Sciences, Sofia, Bulgaria*, Konstantin T. Balashev, *Sofia University, Sofia, Bulgaria*, Nina Kostova, *Bulgarian Academy of Sciences, Sofia, Bulgaria*

1224 **Phase, Microstructure, Mechanical and Wear Characteristics of Sintered Rocks Powders**
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1231 **Effect of Yttria Addition on Mechanical and Tribological Properties of Plasma Nitrided Sintered AISI 316L**
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1269 **Tribological Behavior of Spheroidal Graphite Cast Irons with Nanoadditives**
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1277 **Friction of Thin Multi-component Oxide Films: Experiments and Modeling**
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JM – Joint Mechanics

WE4-JM1 Passive and Active Frictional Joints
ROOM 8 PALERMO • 16:10 – 17:30

Chair: Muzio Gola, *Politecnico di Torino, Torino, Italy*

1165 **Contact Mechanics of Frictional Lap Joint**
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34 **Measurement and Modelling of Interface Stiffness in Frictional Contacts**
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669 **Assessment on Control Strategies of Friction Dampers**
Marcelo Braga dos Santos, Francisco P. Lepore Neto, *Federal University of Uberlândia, Uberlândia, Brazil*

3 **Semi-active Control of Structures Assembled by Bolted Joints**
Lothar Gaul, *University of Stuttgart, Stuttgart, Germany*, Jens Becker, *Moog GmbH, Boblingen, Germany*

Influence of deposition parameters of TiO_2 sprayed films on the abrasive wear resistance

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1. Introduction

Titanium dioxide is a multifunctional material with promising sensing, catalytic, biomedical etc. properties. An increasing interest concerning TiO_2 coatings due to theirs good wear and corrosion resistance, low friction, biocompatibility etc is observed during the last years [1] Titania coatings with good tribological behaviour are prepared by physical methods [2, 3]. These methods require expensive and complicated apparatus and technique or implementation of high temperatures which could destroy the original nanostructure [4]. The chemical techniques (sol-gel and spray pyrolysis) are cheap alternative for deposition of titania coatings. Nevertheless the studies of the tribological properties of chemically deposited TiO_2 films are very scarce [5]. To our knowledge there are only few studies on the tribological properties of TiO_2 coatings deposited by conventional spray method. It is interesting to investigate the possibilities for preparation of titania coatings by spray pyrolysis. Spray pyrolysis is found to be one of the mainstream chemical methods applied for the deposition of thin films in industrial scale. The method is very simple, fast and allows mixing of initial components at a molecular level. Spray pyrolysis is remarkable with its possibility to obtain nanosize thin films [6]. It is known that nanosize coatings show good tribological properties owing to increase in grain boundaries. The grain boundaries play a major role in the deformation of nanocrystalline materials [7]. Aluminum and its alloys are characterized by the great trend to oxidation, low hardness and low wear-resistance at dry friction conditions [8]. In this paper we have obtained for first time TiO_2 coatings by spray pyrolysis on aluminum substrate and studied the effect of deposition conditions on some tribological properties of the coatings.

2. Experimental

2.1. Films deposition and characterization

Aluminium foil plates with thickness 0.3 mm were used as substrates. Titanium chloride dissolved in isopropanol was used as titanium precursor solution. The solution concentration, substrate temperature and spray volume are presented in Table 1. The precursor solution was sprayed onto heated at different temperatures substrate. The deposits were finally treated at 400°C for 1 hour. The phase composition of the samples was studied by X-ray diffraction (XRD, CuK_α-radiation). The mean crystallites sizes of the samples were estimated using the Scherer formula. Scanning electron microscopy (SEM) and Atomic Force microscopy (AFM) were used for morphology observations.

Table 1: Deposition conditions of the coatings

Sample code	Substrate temperature, (°C)	Solution concentration	Volume of spray solution, (ml)
K1	270	0.2 M	25
K2	270	0.2 M	35
K3*	270	0.1 M	35
K4	270	0.1 M	35
K5	350	0.1 M	35
K6	370	0.1 M	35
K7*	270	0.1 M	25

* - $TiCl_4$ was dissolved in mixture of isopropanol and butyl diglycol.

2.2. Wear: Methods of testing

The present paper deals with the study of abrasive wear of TiO_2 coatings on aluminium substrate dry friction conditions (Figure 1). Experimental study of abrasive wear of coatings is realized by means of the test rig TABER ABRASER according to the kinematical scheme „disk-on-disk" (Fig.1). The specimen 1 (the body) with deposited coating 2 is in the shape of disk and is fixed appropriately on carrying horizontal disk 3 drived by electrical motor 4 with a constant rotational speed $\omega = 1[s^{-1}]$=const. The counter-body 5 is an abrasive disk (roller) of special material CS 10 mounted on horizontal axis 6 in the device 8, by means of which is set the desired normal load P in the contact zone K. Thus, the body 1 and the counter-body 5 are located on two crossed axes. Because of the constant rotational speed of the body 1 and the constant nominal contact pressure p_a, the friction in the contact zone K supports constant speed of rotation of the counter-body 5.

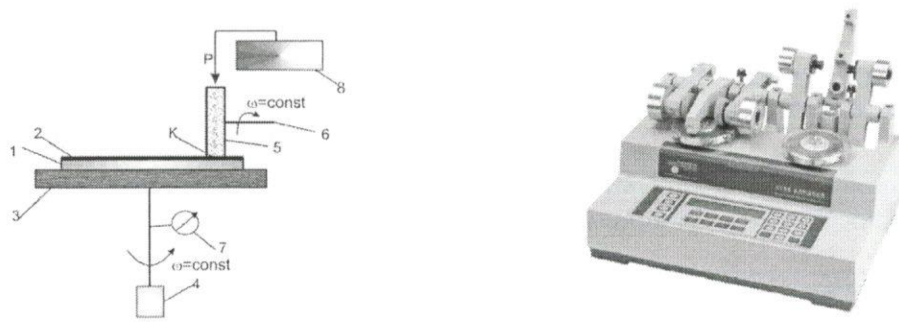


Figure 1 TABER ABRASER – device for study of abrasive wear.

The procedure of the experimental study on abrasive wear is realized in the following sequence of operations:
- clean-up, cleaning of lubricants and drying of the equal specimens. The specimens represent disks of diameter 100 mm and thickness 3 mm with the deposited coatings; - measuring of roughness of the contact surfaces of the specimens before and after wear;
- measuring of specimens mass m_0 before and its mass m_i after a given friction path L by electronic balance WPS 180/C/2 of accuracy 0.1 mg. At every measurement the specimens are cleaned with appropriate solution against static electricity;
- the specimen 1 is fixed on the carrying horizontal disk 3; then the normal load P is set. The friction path L is determined by the number of cycles read by the revolution counter 8.

Abrasive wear for all coatings is obtained by fixed equal operating conditions – nominal contact pressure given with the normal load P, average sliding speed V and parameters of the abrasive surface.

The characteristics of the experiment are given in Table 2.

Table 2 Parameters of wear resistance experiments

Apparent contact area	$A_a = 0.26$ cm^2
Normal contact pressure	$P_a = 17.3$ N/cm^2
Average sliding speed	V = 17.9 cm/s
Abrasive material	CS 10

The following parameters of mass wear are studied:
- Absolute mass m wear;
- Average rate of mass dm/dt, [mg/min] wear;
- Absolute intensity by mass wear $i, [mg/m]$:

$$i = m/S \quad (1)$$

- The friction distance S is calculated by the corresponding number of cycles N and the distance R between the axis of rotation and the mass center of the nominal contact site by the formulae:

$$S = 2\pi RN \quad (2)$$

- Absolute wear resistance by mass I, $[m/mg]$:

$$I = 1/i = S/m \quad (3)$$

3. Results and discussion

The X-ray diffraction analysis of all samples revealed pure anatase crystallographic phase, presented by (101) peak only (Figure 2).

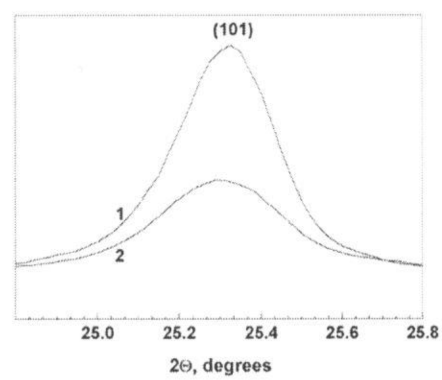


Figure 2 XRD of sample K5 before (1) and after abrasive tests (2)

Table 3 presents comparative wear and crystallite size of the samples.

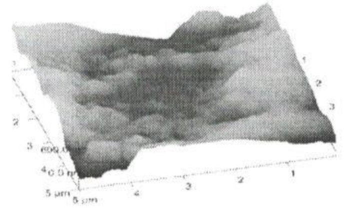
Table 3 Comparative wear and crystallites size of the samples

Sample code	Comparative wear, $\Sigma = I/I_o$		Size of crystallites (nm)	
	After 200 cycles	After 300 cycles	Before tribological tests	After tribological tests
K1	2.56	1.53	32	-
K2	0.15	0.15	36	29
K3*	0.96	0.84		
K4	2.00	1.26	31	26
K5	1.34	1.14	30	24
K6	3.35	2.84	25	19
K7*	4.67	3.52	22	-

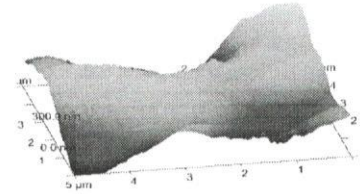
It has to note that the anatase is preserved after 400 cycles of friction. After abrasive tests two effects are observed (i) the crystallites size of all samples are reduced with about 5-7 nm and (ii) larger width of (101) peak. This could be explained with the influence of plastic deformation and as result a generation of defects in the crystal lattice of TiO_2.

The decrease of the crystallite size with increasing of substrate temperature was observed. This effect is in agreement with the concept of Leong et al. based on the precipitation theory [10]. According to this concept, the number and size of the crystals generated from the evaporation of droplets depends on the degree of supersaturation. With rising temperature, the droplet evaporation rate and hence, the degree of supersaturation, increase, which leads to a trend to formation of a large number of nanometer-sized crystallites.

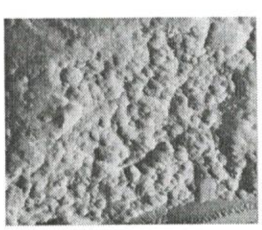
The morphology of the coatings was investigated by both SEM and AFM analyses. The surface of the sample before wear tests is rough (roughness 175 nm; Figure 3-a).



a



b



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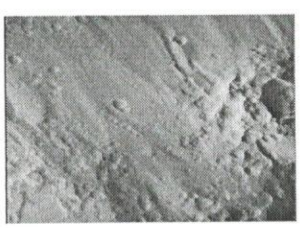

d

Figure 3 AFM photographs of TiO_2 coating (K7) before (a, c) and after 400 abrasive cycles (b, d)

After 400 abrasive cycles the surface becomes considerably smooth (roughness 149 nm; Figure 3-b) with clearly visible signs of plastic deformations (Figure 3-c). Similar behaviour of TiO_2 films, deposited on glass substrate is observed by Zhang et al. [5]. AFM images also revealed that the sample K4 has higher roughness, but lower wear resistance, which may be a result of reduced real contact area between the surfaces of coating and the counterbody. This model is in accordance with the results in [11].

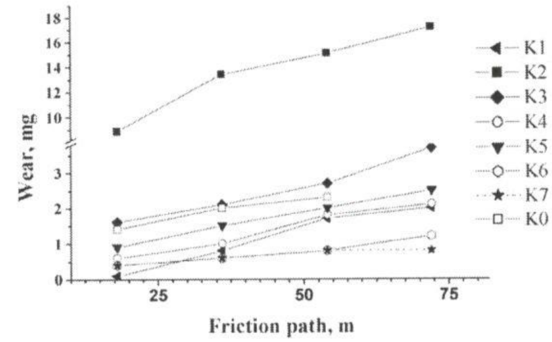

Figure 4 Wear versus friction path

The wear depends on the friction path and increases with the increasing of the crystallites size (Figure 4, sample K2). This may be due to the lower films adhesion to the substrate.

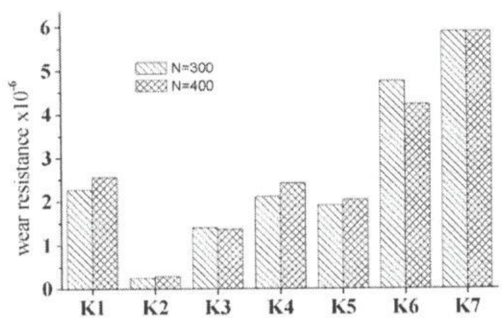

Figure 5 Wear resistances of the samples after 300 and 400 cycles

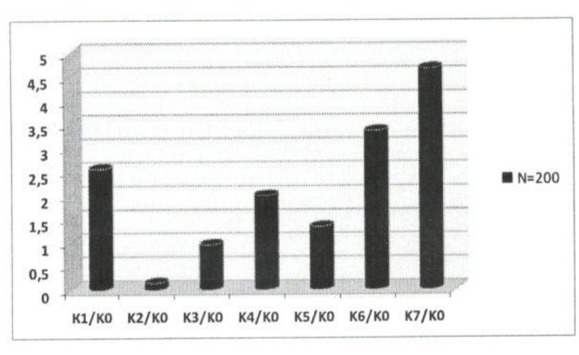

Figure 6 Chart of comparative wear resistance $\varepsilon_{Ki,K0}$

The wear resistance experiments have revealed that the deposition conditions of the TiO_2 coatings have significant influence on their tribological properties.

The increased support temperature and application of solvent with higher boiling temperature leads to a smaller crystallites size. Another factor, influencing the crystallites size is the concentration of titanium precursor. The coatings obtained from 0.1 M solutions possess smaller crystallites, than those, obtained form 0.2M solutions. The highest wear resistance exhibits the coating obtained from 0.1 M solution with butyl diglycol at temperature 270°C. This sample is characterized by constant wear resistance *vs* friction path according to our experimental conditions. According to our results, as a rule TiO_2 coatings with 20-25 nm exhibit higher wear resistance than the coatings with crystallites above 30 nm. This effect is in accordance with the data of Jia et. al. for TiO_2 sol gel coatings [12].

4. Conclusions

The spay pyrolysis method is successfully applied for deposition of nanosize TiO_2 coatings with good tribological properties.

The tribological measurements reveal:

(i) The coatings of TiO_2 increase wear resistance of aluminium substrate.
(ii) Wear resistance depends on the friction path.
(iii) The best coating K7 exhibits a constant wear according our experimental conditions.

The increased support temperature, application of solvent with higher boiling temperature and optimal spray solution volume leads to a smaller crystallites size, which are responsible for the high wear resistance.

5. Acknowledgements

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