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Low friction and wear resistant coating systems on Ti6Al4V alloy

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ABSTRACT

Purpose: Development of an original multiplex hybrid treatment of Ti6Al4V alloy: diffusion hardening+intermediate hard gradient TiC_xN_y layer with use of continuous CAE+top low friction and wear resistant hard amorphous a-C layer with use of pulsed CAE method.

Design/methodology/approach: Ti6Al4V substrates were diffusion hardened with interstitial O or N atoms with use of glow discharge plasma in the atmosphere $Ar+O_2$ or $Ar+N_2$. Next they were deposited with a hard gradient TiC_xN_y layer and with a hard amorphous a-C coating as the top one. The morphology, microstructure, chemical and phase composition, chemical bonds, microhardness and tribological properties during dry friction of the alloy after multiplex treatment have been investigated with use of SEM, EDS, XRD, XPS, Vickers diamond indenter and ball-on-plate test.

Findings: An important increase of hardness of the near surface zone of the Ti6Al4V alloy has been achieved (from ~350VHN to ~1000 VHN), good adhesion between the gradient TiC_xN_y coating and the Ti6Al4V substrate as well as an important decrease of dry friction coefficient (down to ~0.15) and a substantial increase of the resistance to wear (up to two orders of magnitude in comparison with non treated Ti alloy).

Research limitations/implications: The research will be continued on greater number of specimens and against other counterbodies.

Practical implications: It looks like that the Ti alloys can be used as mobile parts of machines due to high resistance to wear and low friction.

Originality/value: A novel original multiplex hybrid treatment of Ti alloys has been developed at the Lodz University of Technology.

Keywords: Surface treatment; Glow-discharge treatment; Duplex treatment; Thick and thin coatings; Gradient coating; a-C:H(Ti) coating; a-C coating; Dry sliding friction; Ball-on-plate test

1. Introduction

Titanium alloys are attractive constructional materials due to low volume density, high specific strength, high resistance to electrochemical corrosion (in particular in sea water) as well as high biocompatibility to the environment of human tissues [1]. They are largely applied in aviation, space, naval and chemical industries as well as in medicine and, according to Bell [1], the 21^{st} century would be the one of titanium in result of novel advanced extraction technologies of this metal. Basic drawback of Ti alloys is their relative low load-carrying capacity as well as their poor tribological properties as, for example, high friction coefficient and proneness to seizure during dry sliding against numerous important technical metals and alloys. Attempts to overcome these drawbacks by hardening of surface and near-surface zone of these alloys with use of interstitial C, N, or O has led only to a limited increase of the resistance to fretting wear and to only a slight decrease of friction coefficient, even though their load-carrying capacity has been increased to a great extent [2-4]. In order to improve radically the tribological properties of Ti alloys Bell et al. [5] have proposed a duplex treatment, in which a

Table 1.
Chemical composition of the substrates [in mass %]

	Al	C	Co	Cr	Cu	Fe	Mn	Mo	O	Sn	Ti	V	W	Zr
Ti6Al4V	6.3	0.14	-	0.2	0.02	0.18	0.1	0.1	0.19	0.1	R*	4.12	-	0.1
T1 HSS	-	0.81	4.5	4.2	-	R*	-	-	-	-	-	1.5	18.5	-

R* - balance

Table 2.
Conditions of the diffusion treatment of the Ti6Al4V substrate in a glow discharge in the atmosphere of Ar+O_2 or Ar+N_2

Atmosphere	Temperature [K]	Ar gas flow [ml·min^{-1}]	Ar partial pressure [Pa]	O_2 or N_2 gas flow [ml·min^{-1}]	O_2 or N_2 partial pressure [Pa]	Potential &current of glow discharge [V]/[A]	Process durability [ks]
Ar + O_2	1223	35	13	6	2	500÷800/0.06÷0.09·	10.8
Ar + N_2	1173	35	13	6	2	500÷800/0.06÷0.09·	28.8

thin, low friction, hydrogenated, diamond-like carbon (DLC) a-C:H co-ating is deposited onto a deep hardened (with use of interstitial O atoms) Ti6Al4V alloy. In result an important increase of a load-carrying capacity as well as a radical increase of tribological properties of the Ti alloy has been achieved**.** Independently, a series of low friction, wear resistant carbon-based coatings has been developed recently. These are, among others, amorphous carbon metal containing, hydrogenated and non-hydrogenated DLC coatings type WC/C or WC(N)/C [6,7] or Cr/C or Cr(N)/C or CrC/C ones [8-10] or (Ti,Cr)CN/C nanocomposite coatings [11] or N doped amorphous carbon a-C:H(N) ones [12] or hydrogenated amorphous magnetron sputtered Ti-containing a-C:H(Ti) monolayer coatings [10] or gradient ones [13]. All of them were well resistant to wear with a very low dry friction coefficient (~0.1 or even less) and could be considered as solid lubricants.

2. Experimental

The disks Ø25.4x6mm cut off from cylindrical bar from Ti6Al4V alloy served as the substrates. For some investigations it was necessary to use cubicoid substrates from grade T1 (18-0-1) high speed steel (HSS) of the dimensions 25x20x10mm as well as very high purity (>7N) Si wafers of the thickness 0.56mm. The chemical specifications of the substrates are given in Table 1. All the substrates were polished and their roughness parameter Ra was less than 0.02µm. The Ti6Al4V substrates first were submitted to diffusion hardening up to the surface hardness ~1000HV0.2 with use of glow discharge plasma in the atmosphere Ar+O_2 or Ar+N_2. The equipment and processing of these treatments have been described in [2] and their parameters used in the present work are given in Table 2. The HSS specimens were quenched and tempered to the hardness 66 HRC. Next the specimens were deposited from the vapour phase with gradient, functional TiC_xN_y coating by means of a conventional cathode arc evaporation (CAE) [14,15] with use of a continuous arc discharge with magnetic filtration of microdroplets onto which thin and hard amorphous carbon a-C coating has been deposited as the top one with use of discontinuous arc discharge. These coatings have been deposited with use of a multipurpose coating unit URM 079 (Fig. 1) equipped with two independent sources for continuous and two for discontinuous arc discharge. Before deposition the specimens were sputtered cleaned with simultaneous use of four independent Ar^+ ion guns at 4kV and 100mA each one at Ar pressure 0.25Pa during 20 minutes after which they were heated with use of the Ti^+ ions of the energy 1÷1.2keV during ~200s in result of switching on the arc discharge and convenient substrates polarisation potential -1.0 kV. Next a thin (~100nm) Ti-layer has been deposited during (~100s) in result of a change of substrate bias to -100V, after which a gradient TiC_xN_y layer has been deposited by means of a controlled gradual change of the flow of the reactive gases (N_2 and/or C_2H_2) from 0.22 sccm and 0 sccm, respectively, at the beginning, to 0 sccm and 0.8 sccm, respectively, at the end of the the time interval 360s (or 2.4 ks). The thickness of the gradient layer was approximately ~150nm (or 0.8µm) respectively and the total pressure in the working chamber during deposition was $2.1\cdot10^{-3}$Pa. Next the gas flow has been shut down, the working chamber has been pumped down to the pressure ~10^{-3}Pa and a thin (~200nm) amorphous a-C coating has been deposited onto the surface of the TiC_xN_y gradient coating by means of a discontinuous CAE process with use of a pure graphite cathode at -300V potential and "zero" bias of the substrates at a frequency of carbon plasma pulses in the range 0.85÷2.45Hz and total number of pulses 30000. After deposition the residual pressure in the chamber was $7.5\cdot10^{-4}$Pa.

3. Results of the investigations

A SEM morphology of the surface of the TiC_xN_y coating deposited onto the Ti6Al4V substrate by means of a continuous CAE process is given in Fig. 2. The microstructure of the two-phase α+β Ti6Al4V substrate after diffusion hardening and coating with ~1µm gradient TiC_xN_y layer is given in Fig. 3. An example of an XRD diffraction pattern from the surface of the thick (~1µm) TiC_xN_y gradient coating on SW18 HSS steel is given in Fig. 4 and a SEM morphology of the fracture of similar coating on Ti6Al4V substrate together with EDS line profiles of Ti, C, N and O elements with use of Ti Kα, C Kα, O Kα and N Kα are given in Fig. 5. XPS "in-depth" profile of a thin (~150nm) gradient TiC_xN_y coating on Ti6Al4V alloy is given in Fig. 6. An overall XPS spectrum from the surface of a thin (~150nm) a-C coating on the gradient TiCxNy layer is given in Fig. 7 together with the C1s peak resolved into 4 components (including the diamond-like sp^3 and the graphite-like sp^2 ones). The results of the ball-on-disk test of dry friction and wear of the complex coating system deposited onto the hardened Ti6Al4V substrate with the hard a-C coating as the top layer against a tempered 0.25" diam. high carbon 100Cr6 bearing steel under the load of 5N and at linear velocity of 5cm·s^{-1} is given in Fig. 8 together with the results of a similar test for the case of a gradient a-C:H(Ti) coating[†] (see pos. [13]) as the top layer instead of the a-C one in the former test (with the aim of comparison).

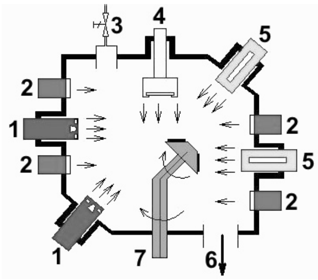

Fig. 1. Scheme of the equipment of the working chamber of a multi-purpose installation for deposition of different PVD coating systems: 1- two independent 4 kW arc guns for continuous CAE process; 2- four independent 4kV Ar ion guns; 3-gas flow control system; 4-10kW mag netron gun; 5- two independent arc sources for discontinuous CAE pro-cess; 6- connection to vaccum pumps; 7- rotary table for specimens with digital position control system

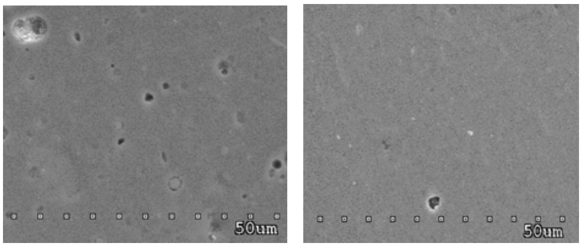

Fig. 2. SEI morphology of the surface of two gradient TiC_xN_y coa-tings deposited by means of a continuous CAE process onto the diffusion hardened Ti6Al4V alloy without (photo on the left) and with magnetic filtering of microdroplets (that on the right)

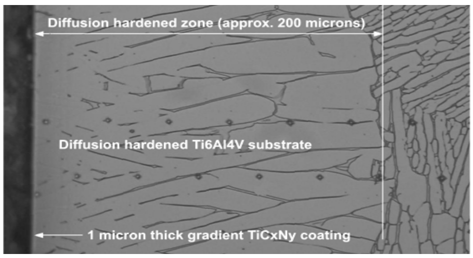

Fig. 3. SEI image of the microstructure of the two-phase α+β Ti6Al4V substrate after diffusion hardening and coating with ~1μm gradient TiC_xN_y layer with use of CAE process

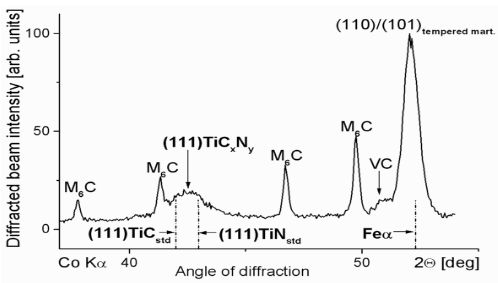

Fig. 4. XRD diffraction profile from the surface of 1μm thick gra-dient TiC_xN_y coating deposited onto tempered T1 HSS substrate

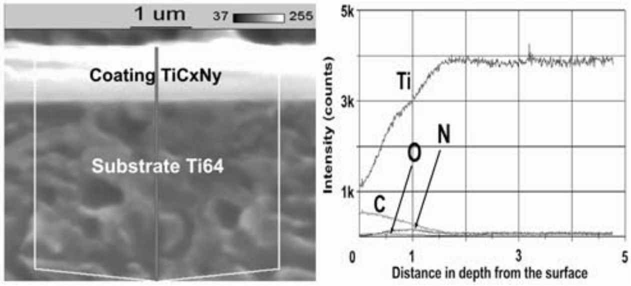

Fig. 5. SEI image (left) of a fracture of the gradient TiC_xN_y coating on diffusion hardened (with oxygen atoms) Ti6Al4V substrate. The arrow is marking an area and direction of the EDS line scan pro-files of concentration of the elements Ti, C, O and N, which are shown on the right hand side

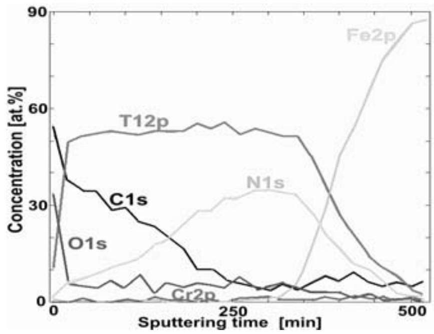

Fig. 6. In depth concentration profiles of a thin (~150nm) gradient TiC_xN_y coating on tempered T1 HSS steel with a continuous change of concentration of carbon atoms from 0 at.% at the substrate to ~50 at. % at the top of the coating and an opposite change of concentration of nitrogen toms: from about 36 at.% to 0 at.%

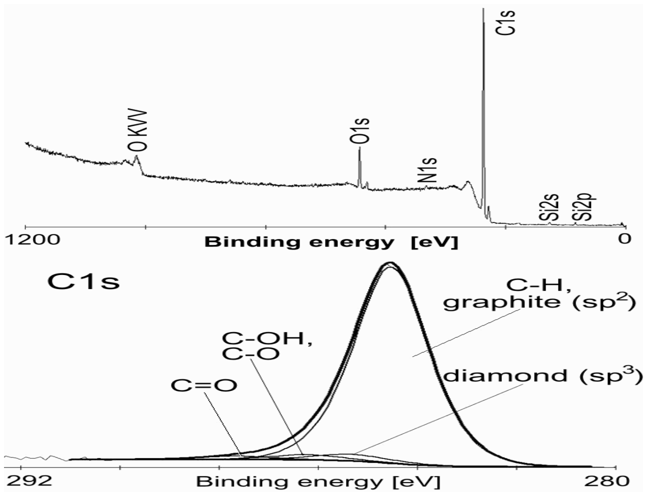

Fig. 7. An overall XPS spectrum from the surface of the amorphous a-C coating deposited by means of a discontinuous CAE process onto the surface of a pure Si substrate (on the top) and the carbon C1s peak from that figure resolved into different components including the diamond-like sp^3 and the graphite-like sp^2 ones (lower down)

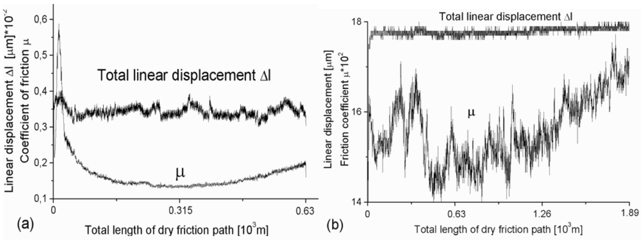

Fig. 8. Dry friction coefficient and wear against a ball from bearing steel of diffusion hardened Ti6Al4V alloy with a gradient TiC_xN_y layer and the amorphous a-C coating as the top layer (on the left) and the same substrate with a gradient a-C:H(Ti)† coating as the top layer (on the right)

4. Discussion of the results

It follows from Figs. 2,3,5 and 6 that the gradient TiC_xN_y coatings adheres well to the Ti6Al4V substrate. In particular it follows from Fig. 6 that it is rather "diffusion bonded" to the T1 HSS substrate. If instead of the HSS steel the Ti6Al4V alloy was used as the substrate this conclusion could be hardly drawn due to superposition of the input from the Ti atoms from the coating with that from the substrate. For similar reasons pure flat Si wafers have been used as the substrates for XPS investigations of amorphous a-C layers deposited by discontinuous CAE process (Fig. 7). In that case carbon atoms from gradient TiC_xN_y coating would influence the form of the C1s peak from C atoms from the a-C layer.

As it concerns the results of the ball-on-disk tests (Fig. 8) it is worth to mention that the total mutual displacement Δl of the steel ball against the surface of the Ti6Al4V disk after multiplex treatment is hardly changing during the test. It means that the total linear wear in the both coatings systems shown in Fig. 8, i.e. with the a-C top layer as well as with the gradient hydrogenated a-C:H(Ti) one, exhibit not only very small friction coefficient, but also a negligeable linear wear (less than 1 μm). Taking into account that the friction path was at least 630m at the load 5N the corresponding wear rate was less than $10^{-16} \cdot m^3 \cdot N^{-1} \cdot m^{-1}$ This relatively very low wear rate (see [8]) allows to consider the both carbon-based coatings as solid lubricants.

5. Conclusions

The following conclusions have been drawn from the investigations performed in the work:

1. The diffusion strengthening of two-phase Ti alloys with use of interstitial O or N atoms is an effective method of increasing microhardness and the load-bearing capacity of these alloys.
2. Due to increase of the interstitial O or N atoms in the near-surface zone there is only single α phase at the surface and the content of the β one is increasing with the distance from the surface.
3. CAE deposited gradient TiC_xN_y coatings are well adhering to the Ti6Al4V substrate and serve a good hard intermediate layers between the Ti substrate and the top hard amorphous a-C layer.
4. The multiplex treatment of the Ti6Al4V alloy (i.e.: hardening with interstitial O or N atoms+CAE gradient TiC_xN_y interlayer+top CAE a-C coating) is a promising way to decrease dry friction coef-ficient against high carbon bearing steel to a value ~0.15 and to increase wear resistance approximately two orders of magnitude in comparison with non-treated or only diffusion treated Ti alloys.

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