Scientific report

on the implementation of the project ***PN-II-ID-PCE-2011-3-1016***
"High Entropy Alloy carbides as next generation coatings - HOPING"
October 2011– October 2016

Introduction

The conventional alloys are based on one principal host element which acts as a matrix, the other elements being added in small percentatges, in order to improve their properties. Apart from the "traditional" alloys, the relatively new intermetallic compounds based on Fe-Al, Ni-Al and Ti-Al binary systems, have been found to possess high specific strengths and thermal resistance, but they have limitted applications due to their brittleness.
In 2004 an alternative approach to alloy design, synthesis and processing has been proposed, based on a composition with at least five principal elements in near-equiatomic ratios, each at 5 – 35 at.% [J.W.Yeh, S.K.Chen, S.J.Lin, et.al., 6 (2004) 299]. In this way it is possible to exploit the merits of each element thus generating the so-called “cocktail effect” [J.W.Yeh, S.K.Chen, S.J.Lin, et.al., 6 (2004) 299]. These alloy systems are known as “high-entropy alloys” (HEA), because their configurational entropy, in the range 1.6 – 2.2 R (R - universal gas constant), exceeds that of an ordinary alloy (1 – 1.1 R). As a result of the combined effects of high mixing entropy, severe lattice distortion (due to the different atomic sizes of the elements) and sluggish diffusion (low efficiency in kinetics), these alloys easily yield the formation of simple and stable solid-solutions phases with FCC or BCC structures, rather than binary or ternary intermetallic compounds, which are usually associated with the brittleness of the material. Up to now, HEAs consisting of rather arbitrary combinations with 5 to 8 constituents of the elements Fe, Cr, Cu, Ni, Co, Mn, Al, Ti, Mo, Nb, Ta, V, Zr, Y and Si have been investigated [J.W.Yeh, Ann.Chim.-Sci.Mat., 31 (6) (2006) 633; T.K.Chen, T.T.Shun, J.W.Yeh and M.S.Wong, Surf.Coat.Technol., 188-189 (2004) 193; C.H.Lai, S.J.Lin, J.W.Yeh and A.Davison, J.Phys.D:Appl.Phys., 39 (2006) 4628; H.H.Cheng, C.H.Lai, S.J.Lin and J.W.Yeh, Ann.Chim.-Sci.Mat., 31 (6) (2006) 723; V.Dolique, A.L.Thomann, et. al., Surf.Coat.Technol., 204 (2010) 1989].
Actually, many metallic HEA phases are known, as bulk and coatings. The HEA carbides belong to a group of nanocomposite multicomponent carbides (HEA-C). It constitutes of transition metals (M), forming strong (A4-A6 groups), or weak (A12-A13 groups) bonds with Carbon, and selected elements from A13-A14 groups, as Al and Si, which are promoting stable properties even at high temperatures. The mixture of strong M-C bonds and weaker M-A bonds in the nanocomposite gives an unique and interesting mixture of metallic and

ceramic properties. The materials can be machinable, are resistant to high temperature oxidation and to thermal chocks, as well as being electrical and thermal conductive.

Objectives

As technology is advancing exponentially, the machines, components, and materials are subjected to increasing extremes of working conditions in terms of friction, wear, temperature, corrosion, etc. Today's high performance devices require high performance new materials with engineered surfaces which can provide additional strength, flexibility, stability, durability, adhesion and protection.

The project is aiming for the development of novel carbide coatings, based on HEA-C multicomponent system with high enthropy, lubricant, with high surface energy and high corrosion resistance. The fundamental research approach will be complementary with the tests of the new coatings in adverse conditions mimiking severe working conditions.

Two essential Objectives will be carried out:

O1. New recipes /technologies for synthesis of functional HEA-C coatings, based on an intricate knowledge of the bond strengths, formation energies and optimum value of valence electron concentration, achieved by properly adjusting the element choice and concentration.

O2. A test/validation program including a set of mechanical, tribological, corrosion and electrical tests, at ambiental and high temperatures for the evaluation of the functional coatings. All the extensive tests carried out as part of this objective will clearly identify areas of potential directions toward the use of the HEA-C coatings. In this way there will be assessed different functional surfaces with desirable properties for operation in specific applications.

Work-plan and Results

Derived from the main objectives, the project comprises four work-packages (WP) with the associated tasks (T), foreseen to be developed in parallel thorough-out the entire project duration. The first two WPs are associated with the deposition and subsequent characterisation of the newly developed coatings. The third WP is dealing with the project management, IPR issues and international networking, while the last one is related to dissemination activities (results publication and communication), as presented in the Table bellow.

WP1 Deposition of various HEA-C coatings by magnetron sputtering technique	**WP2 Complex coatings characterization**
T.1.1 Investigation of the reactive plasma by Optical Emission Spectroscopy	**T.2.1** Coatings characterization for composition, crystalographic structure, morphology
T.1.2 Growth studies on monocrystalline substrates (MgO, Si)	**T.2.2** Mechanical and tribological properties investigation and assessment
T.1.3 Optimized deposition recipes for over, under and stoichiometric HEA-C coatings	**T.2.3** Corrosion behavior investigation; corrosion resistance assessment
T.1.4. WP1. Deposition of various HEA-C coatings by magnetron sputtering technique on different substrates, targeting specific applications	**T.2.4** High temperature stability assessment
WP3 Management of the project, including the intellectual property rights (IPR) and networking with scientist researchers working abroad.	**WP4 Results dissemination at international level**
T.3.1. Project management	**T.4.1.** Papers submission to ISI quoted journals
T.3.2. Patents submission to the Patent Office	**T.4.2.** Communications at international conferences
T.3.3 Exploitation strategy (international networking, SME involvement), project proposals submission	

WP1 – Deposition of various HEA-C coatings by magnetron sputtering technique & WP2 – Complex coatings characterization.

T.1.1 – Investigation of the reactive plasma by Optical Emission Spectroscopy

Plasma discharges in methane or methane–argon gas mixtures are widely used in PVD processes, aiming to coat surfaces with metal carbides. In this study we investigated by optical emission spectroscopy (OES) the excited and ionized species present in a magnetron discharge used for the reactive deposition of ZrC films in a mixture of argon and methane. The aim of this investigation was to study the modification of the plasma due to He addition in the reactive atmosphere.

Summarizing, the analyse of the optical emission spectroscopy data permitted to find an optimum interval of deposition, in terms of the flux of the discharge gases, as follows:

i. the methane mass flow should not be higher that the mass flow of (Ar+He);

ii. the addition of He has a positive impact on the methane decomposition;

iii. an optimum value for the He dilution in Ar was determined, for which an increase of Zr ions abundance was obtained.

- Optical emission spectroscopy study on He addition in an Ar/CH4 reactive DC magnetron discharge aiming for ZrC films deposition, I. Pana, C. Vitelaru, M. Braic, International Conference on Phenomena in Ionized Gases – ICPIG, 26-31 July 2015, Iasi, Romania
- Tunable optical properties of thin films by OES monitoring in a reactive RF magnetron plasma, I. Pana, C. Vitelaru, N. C. Zoita, M. Braic, Plasma Processes and Polymers,13 (2016) 208-216, doi: 10.1002/ppap.201400202

T.1.2 Growth studies on monocrystalline substrates (MgO, Si)

T.1.2.1 + T.2.1 Hetero-epitaxial growth studies of TiC thin films on MgO (100)

The films were deposited by reactive magnetron sputtering of a Ti target in Ar and CH_4 atmosphere, using the AJA Orion equipment.

It was observed the influence of the film thickness on the structure, morphology and electrical resistivity of the heteroepitaxial TiC coatings deposited at 800 ^{0}C on (100) MgO substrates.

- Influence of film thickness on structure and electrical properties of epitaxial TiC/MgO films deposited by reactive magnetron sputtering, N. C. Zoita, V. Braic, M. Danila, M. A. Vlaicu, M. Braic, Journal of Crystal Growth, 389 (2014) 92-98.

It was studied the growth of TiC films on (100) MgO substrates at low temperature (100 ^{0}C). There were assesed the crystalographic strucure, the surface morphology and the electrical resistivity.

- Hetero-epitaxial growth of TiC films on MgO(001) at 100 °C by DC reactive magnetron sputtering,M.Braic, N.C. Zoita, M. Danila, C.E.A. Grigorescu, C. Logofatu, Thin Solid Films 589 (2015) 590-596, doi:10.1016/j.tsf.2015.06.021.

T.1.2.2 + T.2.1 – Growth studies of carbides on monocrystalline substrates (Si)

There were studied the peculiarities of HEA-C: (CrCuNbTiY)C coatings growth on Si(100) substrates, at different substrate temperatures (80, 300, 500 si 650 ^{0}C).

The increase of the deposition temperature de determined a decrease of the surface roughness at 500 °C and at 650 °C, due to enhanced mobility on the coating suraface, as reported also for other multicomponent coatings [C.H. Lai et al., Surf. Coat. Technol. 201 (2007) 6993–6998), as well as due to growth by repeated nucleation [I. Petrov, P.B. Barna et al., J. Vac. Sci. Technol. A 21 (2003)117–128; J.R. Heffelfinger, C.B. Carter, Surf. Sci. 389 (1997) 188–200]. We considera that the growth by repeated nucleation is specific for multicomponent and HEA-C coatings, due to the random position of dissimilar atoms in the crystallyne lattice. Similar phenomena were evidenced in TiSiC-Ni coatings, as documented in:

- Growth and Characterization of Arc Evaporated TiSiC–Ni Coatings, M. Balaceanu, A. C. Parau, M. Braic, A. Vladescu, C. R. Luculescu, C. Logofatu, V. Braic, Tribology Letters, 58 (2015) 43: 1-9; doi: 10.1007/s11249-015-0521-6
- Effects of Zr, Nb or Si addition on the microstructure, mechanical and corrosion resistance of TiCN hard coatings, L. Constantin, M. Braic , M. Dinu, M. Balaceanu, V. Braic, C. Farcau, A. Vladescu, Materials and Corrosion 67 (2016) 929-938, doi: 10.1002/maco.201508737

We underline that the details observed in the morpholgy of the coatings, as determined by their deposition conditions, are directly influencing their mechanical, tribological, anti-corrsion properties, in direct connection with their posssible application.

- Effects of substrate temperature and carbon content on the structure and properties of (CrCuNbTiY)C multicomponent coatings, V. Braic, A. C. Parau, I. Pana, M. Braic, M. Balaceanu, Surface and Coatings Technology, 258 (2014) 996–1005, doi: 10.1016/j.surfcoat.2014.07.044

T.1.3. Optimized deposition recipes

T.1.3.1 + T.2.1 HEA metallic films

The aim of the study was to find out the factors controlling phase formation in TiZr-based HEA metallic films. We deposited films made with 3–5 constituents, by magnetron sputtering co-deposition from multiple single-element targets. We selected the TiZr-system as a binary base system because Ti and Zr are completely miscible in the solid state, forming a solid solution comprising elements with quite different radii, with well-known structure and characteristics [B.T. Wang et al., J. Nucl. Mater. 420 (2012)501].

- Solid solution or amorphous phase formation in TiZr-based ternary to quinternary multi-principal-element films, M. Braic, V. Braic, A. Vladescu, C. N. Zoita, M. Balaceanu, Progress in Natural Science: Materials International, 24 (2014) 305 -312, doi: 10.1016/j.pnsc.2014.06.001

T.1.3.1 + T.2.1 - T.2.3 Deposition and complex characterization and multicomponent carbide coatings

I. Deposition and complex characterisation of (TiZrNbHfTa)C coatings

The first study aimed to assess the influence of Hf in a known biocopatible compound: ZrCN. Two series of overstoichiometric coatings, having (C + N)/(Zr + Hf) ratios of about 2.0 and 3.5, respectively, have been prepared. The research carried out showed that the anticorrosive and biocompatible film characteristics depended on the non-metal/metal ratio. An improved corrosion behavior was found by adding Hf to the basic ZrCN structure. For the ZrHfCN coatings, the increase in non-metal/metal ratio led to a better corrosion resistance. Both coating series exhibited a good biocompatibility at in vitro tests. After 5 days in culture, the osteosarcoma cells were well developed and already presented an ideal fusiform shape. The ZrHfCN coating with (C + N)/(Zr + Hf) ~ 3.5 presented the highest cell viability, with dense and well-defined actin bundles, and strong contacts with the surface, being favorable for osteosarcoma cells' colonization. In conclusion, due to their high corrosion-wear resistance and good biological properties, the ZrHfCN coatings with high non-metal/metal ratio could be a promising solution for improving the characteristics of Ti6Al4V alloy used in biomedical applications.

- Corrosion resistance, mechanical properties and biocompatibility of Hf-containing ZrCN coatings, C.M.Cotrut, V.Braic, M.Balaceanu, I.Titorencu, M.Braic, A.C.Parau, Thin Solid Films, 538 (2013) 48-55, doi:10.1016/j.tsf.2012.12.100

The coatings were deposited by magnetron sputtering using Ti, Zr, Nb, Hf and Ta cathodes. Two types of coatings were deposited: under-stoichiometric (TiZrNbHfTa)C-1 and stoichiometric (TiZrNbHfTa)C-2.

The research carried out showed that the mechanical, tribological and anticorrosive characteristics of biocompatible Ti6Al4V alloy could be significantly improved by using (TiZrNbHfTa)C carbide protective coatings. The investigated coatings were found to possess high hardness, low friction coefficient and superior wear-corrosion resistance, as well as good biocompatible properties.

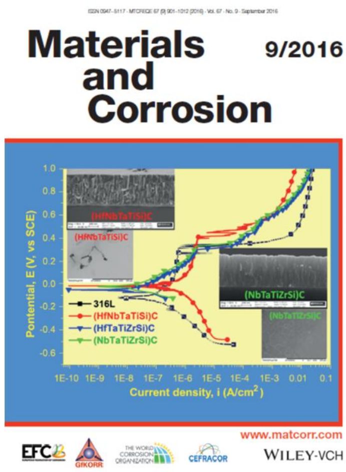
- Characterization of multi-principal-element (TiZrNbHfTa)N and (TiZrNbHfTa)C coatings for biomedical applications, V. Braic, M. Balaceanu, M. Braic, A. Vladescu, S. Panseri, A. Russo, Journal of the Mechanical Behavior of Biomedical Materials, 10 (2012) 197-205.

II. Deposition and complex characterisation of (HfNbTaTiSi)C, (HfTaTiZrSi)C and (NbTaTiZrSi)C coatings

Three types of multi-principal carbide coatings – (HfNbTaTiSi)C, (HfTaTiZrSi)C and (NbTaTiZrSi)C – containing, apart from carbon and silicon, four elements selected from five transition metals known as biocompatible (Hf, Nb, Ta, Ti, Zr), were investigated as possible candidates for biomedical applications.

Based on the current investigation, the following conclusions can be drawn:

1. The coatings, with atomic concentrations of metals, Si and C in the ranges 8.2–10.5 at.%, 6.9–7.2 at.% and 49.5–50.3 at.%, respectively, contained FCC solid solution phases, with crystallite sizes of 9.5–12.6 nm.
2. Electrochemical corrosion tests in simulated body fluid (pH7) at 37 °C revealed that all the investigated coatings showed superior corrosion behaviour compared to the 316L steel in terms of electrochemical parameters (open circuit, corrosion and breakdown potentials, corrosion current density, polarisation resistance and weight loss).
3. The (NbTaTiZrSi)C coating exhibited the highest corrosion resistance, being a suitable candidate to be used as protective film in a biomedical applications.



Front cover of the journal issue with the graphical abstract of our paper:

- In vitro corrosion resistance of Si containing multi-principal element carbide coatings, M. Dinu, I. Pana, V. Braic, F. Miculescu, M. Balaceanu, A. Vladescu, M. Braic, Materials and Corrosion 67 (2016)908-914, doi:10.1002/maco.201508788.

III. Deposition and complex characterisation of (TiZrNbTaHf)C and (TiZrNbSiHf)C coatings

The study explored the possibility to improve the biocompatibility of the (TiNbZrTaHf)C coating through replacement of either Ti or Ta by Si. The coatings were deposited by reactive magnetron sputtering in an Ar+CH_4 mixed atmosphere. Considering the important role of electrostatic interactions between cells and biomaterial surface in cell attachment, the effects of surface charge as characterized by electrical potential and work function, on coatings' biocompatibility was examined. A significant correlation between electrical potential, work function and coating biocompatibility, as derived from osteoblasts viability and attachment to coatings surfaces, was found. Consequently, either the electrical potential or the work function are proposed as relative predictors for biocompatible characterization of the investigated coatings. Among the coatings, (TiZrNbSiHf)C, with low electrical potential and the high work function, exhibited the best biocompatible properties.

- In vitro biocompatibility of Si alloyed multi-principal element carbide coatings, A. Vladescu, I. Titorencu, Y. Dekhtyar, V. Jinga, V. Pruna, M. Balaceanu, M. Dinu, I. Pana, V. Vendina, M. Braic, Plos One, doi:10.1371/journal.pone.01611511.

IV. Deposition and complex characterisation of multifunctional multicomponent carbide coatings

The aim of the study was to assess the influence of a specific element on the functional characteristics of multicomponent carbide coatings.

A. TiSiC-Ni coatings

The aim of this paper was to further investigate the effects of a weak carbide-forming metal (Ni) addition to TiSiC coatings. This choice was motivated by the existing studies [U. Jansson, and E. Lewin, Thin Solid Films 536, 1 (2013); M. Lindquist, O. Wilhelmsson, U. Jansson, and U. Wiklund, Wear 266, 379 (2009)] which demonstrated that the addition of a weak carbide forming element in a carbide coating led to the grain refinement and favoured the formation of surface layers containing graphite carbon, with beneficial effects on friction behaviour.

Summarizing, the study revealed that alloying TiSiC with Ni resulted in the grain refinement, decrease in the stress level, enhanced adhesion to steel substrate and superior tribological characteristics. The beneficial effects of Ni addition depended on Ni content, the addition of Ni in moderate purcetages (<7.5%) gives the best results, as no Ni segregation was evidenced. The specific features of the wear tracks indicated that the dominant wear mechanism under dry sliding conditions is essentially controlled by the debris adhesion and oxidation.

- Growth and Characterization of Arc Evaporated TiSiC–Ni Coatings, M. Balaceanu, A. C. Parau, M. Braic, A. Vladescu, C. R. Luculescu, C. Logofatu, V. Braic, Tribology Letters, 58 (2015) 43: 1-9; doi: 10.1007/s11249-015-0521-6.

B. TiSiC-NiC multilayered coatings

The goal of the present work was to investigate the main characteristics of a novel type of carbide based non-isostructural multilayer, namely TiSiC/NiC.

The deposited multilayer coatings exhibit a laminate structure with stacking of TiSiC and NiC alternate layers. The bilayer period and the thicknesses of the individual layers estimated from the SEM image were of 9.8 nm, 5.5 nm (TiSiC) and 4.3 nm (NiC), respectively.

The properties of the multilayers significantly depended on the bilayer period Λ, the best performance being obtained for the coating with Λ = 4.8 nm (TiSiC/NiC-720). When compared to the

TiSiC monolithic coating, the major benefits brought by the multilayered system TiSiC/NiC-720 were: reduction of stress level from -3.12 to -0.88 GPa, adhesion enhancement from 36 to 57 GPa, diminishment of friction coefficient from 0.38 to 0.17 and decrease of wear rate from 2.9 to 0.66 x 10^{-6} $mm^3N^{-1}m^{-1}$.

To conclude, the TiSiC/NiC coatings with appropriate thicknesses of the individual layers appear to be promising candidates to be applied on various parts and tools that work under severe wear and corrosion conditions.

- Investigation of multilayered TiSiC/NiC protective coatings, A. Vladescu, M. Braic, M. Balaceanu, A. C. Parau, M. Dinu, Vacuum 120 (2015) 60-66, doi:10.1016/j.vacuum.2015.06.019SiC.

C. Effects of Zr, Nb or Si to TiCN coatings

In this study, alloying elements of Zr, Nb and Si have been added to a TiCN ternary carbo-nitride compound. High C/N coatings were selected, because of their superior tribological performance in both dry, and corrosive environments. The improved tribology can be attributed to the high carbon content in the coating, which leads to the formation of an amorphous free carbon phase. It also results in increased grain boundaries length impeding corrosive attack. The selected coatings are investigated to be used as protective coatings for both tribological applications in dry environments and for components and parts that works under corrosive conditions.

Summarizing, stoichiometric TiZrCN, TiNbCN and TiSiCN coatings, with Zr, Nb or Si as alloying elements, with C/N ratio of ~ 0.5 were deposited. By Zr, Nb or Si addition into the TiCN structure, the texture coefficient TC(111) increases, indicating the strong (111) preferred orientation in these coatings. The results demonstrate the beneficial effects of incorporating Zr, Nb or Si in the basic structures of TiCN coatings, as follows: all alloyed coatings exhibited decreased stress and increased adhesion to the metallic substrate; TiNbCN coating showed the highest resistance to corrosion attack in 3.5 % NaCl, due to its high adhesion to the steel substrate and to the lowest roughness; Ti based carbonitride coatings with alloying elements are suitable coatings to reduce the corrosion processes of M2 HSS in NaCl aggressive environment.

- Effects of Zr, Nb or Si addition on the microstructure, mechanical and corrosion resistance of TiCN hard coatings, L. Constantin, M. Braic , M. Dinu, M. Balaceanu, V. Braic, C. Farcau, A. Vladescu, Materials and Corrosion 67 (2016) 929-938, doi: 10.1002/maco.201508737.
- TiSiC, TiSiC-Zr and TiSiC-Cr coatings - corrosion resistance and tribological performance in saline solution, A.C. Parau, C. Vitelaru, M. Balaceanu, V. Braic, L. R. Constantin, M. Braic, A. Vladescu, Tribology Transactions, 59 (2016) 72-79, doi: 10.1080/10402004.2015.1077406.

The coatings were also deposited on stainless steel 316L, and investigated for their tribological in dry atmosphere, at ambient temperature and at 250 ^{0}C. The results of the tribological tests were expressed in terms of the change of coefficient of friction (COF) versus time, and wear rate (K). The following conclusions can be drawn from the study:

- Zr, Nb and Si alloying elements in the film composition were in the range 2.9 – 9.6 at. %.
- The coatings exhibited f.c.c. solid solutions and the (111) preferred orientation.
- All the coatings had a good adhesion to the metallic substrate, critical loads of 20 – 30 N being measured. The best adhesion was found for the TiNbCN coating.
- Ti based coatings with Nb or Si alloying elements proved to be resistant to corrosive attack in 3.5 % NaCl. The TiNbCN coating was found to have the best corrosion resistance, due to the low residual stress and high adhesion to the substrate.

- Coatings improved the friction coefficients across all experimental parameters.
- The wear mechanism was found to be dominated by abrasive and oxidative processes.
- The best wear resistance was detected for the TiCN at 250°C and TiNbCN at 23°C .
    - Corrosion and tribological performance of quasi-stoichiometric titanium containing carbo-nitride coatings, C.I. Pruncu, M. Braic, K.D. Dearn, C. Farcau, R. Watson, L.R. Constantin, M. Balaceanu, V. Braic, A. Vladescu, Arabian Journal of Chemistry, (2016), http://dx.doi.org/10.1016/j.arabjc.2016.09.009.

Another study was aiming to investigate the influence of the carbon rich gas (methane or acetylene) on the structural, mechanical and tribological properties of TiSiC-Cr coatings. It was found that the coatings derived from C2H2 outperformed those prepared in CH4 plasma in all of the relevant film characteristics (microstructure, hardness, friction and wear performance). The findings suggest that the source gas type should be considered as a key experimental parameter in addition to the gas pressure, cathode current and the substrate bias voltage. The experimental results demonstrate the significant role of the hydrogenated carbon phase played in determining the properties of the coatings, wherein the films deposited in C2H2 atmosphere showing a significantly higher carbon content and hence superior properties. It is to be mentioned the state of super hardness obtained (H > 40 GPa) for the Cr – alloyed TiSiC coatings when C2H2 was employed as the precursor gas. Further for both the coating types, hardness, friction and the wear characteristics were improved with increasing the reactive gas flow rate (or carbon content). For the coatings deposited from CH4, adhesive and oxidative processes were found to be dominant in the wear mechanism, while for those prepared from C2H2, a mild polishing wear was observed. A higher concentration of a-C:H phase, and their possible homogeneous distribution around the grain boundaries are proposed as the main reason for the significant enhancement of the overall properties.

- A comparative study of the structural, mechanical and tribological characteristics of TiSiC-Cr coatings prepared in CH_4 and C_2H_2 reactive atmosphere by cathodic vacuum arc, M. Braic, A. Vladescu, M. Balaceanu, C. Luculescu, S. C. Padmanabhan, L. Constantin, M. A. Morris, V. Braic, C. E. A. Grigorescu, P.Ionescu , M. D. Dracea, C. Logofatu, Applied Surface Science, 400 (2017) 318–328, doi: 10.1016/j.apsusc.2016.12.160

V. Deposition and complex characterisation of (CuSiTiYZr)C coatings

The aim of this study was to investigate the characteristics of a novel type of HEA-based films, namely (CuSiTiYZr)C.

To sum up, the electrochemical tests showed that, as compared to the ternary (TiZr)C coatings, the (CuSiTiYZr)C coatings are more resistant to corrosion in NaCl solution. The protective character of the coatings improves with increasing carbon content. Taking into account all the parameters for the evaluation of the corrosive behaviour, it appears that the best systems are the (CuSiTiYZr)C-2 and (CuSiTiYZr)C-3.

- Deposition and characterization of multi-principal-element (CuSiTiYZr)C coatings, M. Braic, M. Balaceanu, A. Vladescu, C. N. Zoita, V. Braic, Applied Surface Science, 284 (2013) 671-678.

VI.* Deposition and complex characterisation of *(CrCuNbTiY)C coatings

(CrCuNbTiY)C multi-component coatings with two different carbon contents (C/metal ratio of about 1.1 and 2.7) were prepared by co-sputtering of Cr, Cu, Nb, Ti and Y targets in an Ar + CH4 reactive atmosphere. The (CuSiTiYZr)C coatings exhibited amorphous structures. For all the coatings, an increase in the carbon content led to an improvement to the film characteristics. This result was considered to be the effect of the formation and development of an amorphous free-carbon phase. As compared to the (TiZr)C coatings with similar carbon content, the MPEs exhibited only slightly improved hardness, adhesion and friction performance, but clearly superior corrosion and wear resistance. Of the investigated coatings, the highest hardness (29.5 GPa), the smallest wear rate (1.89 × 10−6 mm3 N−1 m−1) and the lowest friction coefficient (~0.15) were determined for the MPE coating with C/Me* ratio of about 1.3. Due to their superior properties such as good corrosion – wear resistance and low friction, the multi-principal-element carbide coatings, particularly (CuSiTiYZr)C, could be successfully used as protective coatings in various industrial applications.

- Effects of substrate temperature and carbon content on the structure and properties of (CrCuNbTiY)C multicomponent coatings, V. Braic, A. C. Parau, I. Pana, M. Braic, M. Balaceanu, Surface and Coatings Technology, 258 (2014) 996–1005, doi: 10.1016/j.surfcoat.2014.07.044

WP3 – Management othe project

T.3.1 – Project management

Management of the project activities

The project web page - created and continuously up-dated

A MsC student and a PhD student were selected and hired as part of the project team.

T.3.2. Pending patents:

A/00833/16.11.2012: High entropy alloy carbide coatings for joint prosthesis, M.Braic, V. Braic, M. Balaceanu, A. Vladescu

A/00721/03.10.2013: Tribological and corrosion resistant high entropy alloy carbide coatings, M. Braic, V. Braic, A. C. Parau

A/00754/18.10.2013: Biocompatible coatings based on high entropy alloy carbides for surgical instruments and for movable couples in articular joints, M. Braic, V. Braic, A. C. Parau

A/00893/25.11.2013: Multilayered coatings for tribological applications at high temperatures, M.Braic, V. Braic

A/00865/19.11.2015: Multicomponent wear and corrosion resistant ZrC based coatings containing Si and other transition metals, A.Vladescu, M.Balaceanu, V. Braic, A.Parau

T.3.3 – Exploitation strategy, international networking

Proposals for international projects:

Novel Bio-materials for Medical Implants – BIOMEDICI, within the call FP7 NMP.2012.2.2-1. Romanian project leader: M. Braic.

“WHIP”, within the call for Joint Research Projects with France – PN-II-ID-JRP-2012. Romanian project leader: M. Braic

ENV-PHOTO-SENS, within the call SEE - EEA Research Programme 2014. INOE 2000 project leader: V. Braic

Bilateral project: Romania – South - Africa, within the 2014 call for bilateral projects. Romanian project leader: M. Braic, financed 2016

HybrBioScaf, within the call ERA.Net RUS Plus Joint Call for S&T projects- 2014. The team of the HOPING project is part of the proposed project team, financed 2016

Multi-site infrastructure INOVA-OPTIMA", within the call POSCCE-A2-O2.2.1-2013-1; project running from 08.2014. Project leader: V. Braic

TANDEM, within the call M-ERA.Net Joint Call for S&T projects- 2015, financed 2016.

GESNAPHOTO, within the call M-ERA.Net Joint Call for S&T projects- 2015, financed 2016

Team leader - member of scientific committees of international conferences:

- E-MRS Spring 2012, Simp. „C-or N-containing nanostructured thin films", Strasbourg, Franta
- IX-th Conf. Int.„Nanosciences & Nanotechnologies", July 2012, Thessaloniki, Greece
- IVC-19 International Vacuum Congress, 9-13 September 2013 Paris, France
- X-th Conf. Int.„Nanosciences & Nanotechnologies", July 2013, Thessaloniki, Greece
- XI-th Conf. Int.„Nanosciences & Nanotechnologies", July 2014, Thessaloniki, Greece
- ICTF-16, October 2014, Dubrovnik, Croatia.
- XII-th Conf. Int.„Nanosciences & Nanotechnologies", July 2015, Thessaloniki, Greece
- 4th Magnetron, Ion processing & Arc Technologies European Conference; 14th International Symposium on Reactive Sputter Deposition, December 2015, Paris, France.
- XIII-th Conf. Int.„Nanosciences & Nanotechnologies", July 2016, Thessaloniki, Greece
- E-MRS Spring 2016, Symp. „C-or N-containing nanostructured thin films", Strasbourg, France.

Main organizer in international conferences

- Symposium G: "Carbon- or nitrogen-containing nanostructured thin films" desfasurat in cadrul conferintei E-MRS Spring Meeting 2014, Lille, France
- Tutorial " Thin Films Growth by PVD Techniques - Tips & Hints" organizat in cadrul Conferinte E-MRS Spring Meeting 2014, Lille, France
- Symposium I (Functional oxynitride films for sustainable development) in cadrul conferintei internationale E-MRS Spring 2016, 2-6 Mai 2016, Lille, France.

Team leader - Guest editor to Elsevier journals:

- "Thin Solid Films", Volum apeared April 2015
- "Surface and Coatings technology" - to apppear April 2017.

WP4 – Dissemination

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