



## STUDY OF ZrO<sub>2</sub>/Co-DEPOSITION WITH COBALT FROM CHLORIDE ELECTROLYTE

Lidia BENE<sup>1</sup> Florentina Simona SORCARU<sup>1</sup>  
Pierre PONTIAUX<sup>2</sup>, Francois WENGER<sup>2</sup>

<sup>1</sup>Dunarea de Jos University of Galati, Competences Center: Interfaces - Tribocorrosion and Electrochemical Systems (CC - ITES), Romania.

<sup>2</sup>Ecole Centrale Paris. Laboratoire Génie des Procédés Matériaux (LGPM). France.  
email: [Lidia.Benea@ugal.ro](mailto:Lidia.Benea@ugal.ro)

### ABSTRACT

*The metal-matrix composites are materials in which the properties of a metallic host material are modified with addition of a second phase (ceramics) by electrodeposition process. The second phase can be hard oxides or carbides particles or diamond, or solid lubricants or even liquid containing microcapsules. Most composite coatings contain micron-sized particles. The major challenges with the codeposition of second phase particles are the achievement of a high level of codeposition and avoiding the agglomeration of particles suspended in the electrolytes. The poorly homogeneous distribution of second phase particles in the metallic matrix can be detrimental to the mechanical properties. This work shows the most recent results regarding the influence of ZrO<sub>2</sub> bioceramic dispersed in the cobalt matrix during electroplating process from a chloride cobalt electrolyte. The ZrO<sub>2</sub>/Co composite coatings were electrodeposited from a suspension of ZrO<sub>2</sub> particles (mean diameter 10µm) in aqueous cobalt chloride electrolyte. Suspension was prepared by adding 20 g/L ZrO<sub>2</sub> particles into solution. Co-deposition of dispersed micro sized particles with cobalt during electroplating process influences the structure and surface morphology of composite coatings obtained. The pure cobalt coating has a rather regular surface, whereas the composite coatings surface has fine different disturbed structure. The composite coating thickness increases with increasing the current density, whereas the content of ZrO<sub>2</sub> particles inside the cobalt matrix decreases with current density.*

KEYWORDS: ZrO<sub>2</sub> particles, electrodeposition, composite coatings, cobalt.

### 1. Introduction

Metal composite materials have found application in many areas of daily life for quite some time. These materials are produced in situ from the conventional production and processing of metals. These innovative materials open up unlimited possibilities for modern material science and development, the characteristics of MMC can be designed into the material, custom-made, dependent on the application.

The advantages of the composite materials are only realized when there is a reasonable cost-performance relationship in the component production. The use of a composite material is obligatory if a special property profile can only be achieved by application of these materials [1-8].

Biomaterial applications make use of all classes of material, metals, ceramics, polymers and composites, divided roughly into three user types. These are:

- (i) inert or relatively inert with minimal host response,
- (ii) bioactive which actually stimulate bonding to the surrounding tissue and
- (iii) biodegradable which resorb in the body over a period of time.

Metals are generally chosen for their inert qualities whereas ceramics and polymers may offer bioactivity or resorption. Composites could combine the properties of metals with ceramics or metals with polymers. The metal-matrix composite coatings are materials in which the properties of metallic host material are modified with addition of a second phase (ceramics, polymers, etc.) by electrodeposition

process [9-15]. Cobalt favors wear resistance at high temperature as it increases the amount of cobalt, the temperature increases and the use of the material. Property due to cobalt crystallographic structure: cobalt crystallizes in cubic structure with girls under 417°C and centered in a hexagonal structure over 417°C [3].

Cobalt is the most widely material for protection of steel against corrosion. Cobalt is more corrosion resistant than steel in most natural atmospheres, the exceptions being ventilated indoor atmospheres where the corrosion of both steel and cobalt is extremely low and certain highly corrosive industrial atmospheres. Electrodeposition offers rigid control of film thickness, uniformity and deposition rate and is especially attractive owing to its low equipment cost. Due to the use of an electric field, electrodeposition is particularly suited for the formation of uniform films on substrates of complicated shape, impregnation of porous substrates and deposition on selected areas of the substrates [4].

Good deposition depends mainly on the nature of bath constituents. Generally, a plating bath contains conducting salts, buffering agents, complexing agents and metal ions. The action of these complexing agents is specific and depends on pH, nature of anion, temperature and other ingredients of the medium. Too many ingredients cause difficulties in maintaining the operating parameters of the bath solution during the plating process. There are many studies on zirconium oxide devoted to extensive research on corrosion resistance [13].

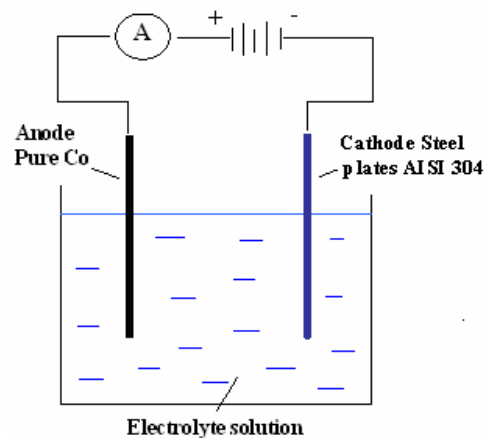
Zirconium oxide, ZrO<sub>2</sub>, is considered nowadays one of the most important ceramic materials in modern technology. It has a wide range of industrial applications because of the excellent combination of high flexural strength (~1 GPa) and good fracture toughness, together with its stability at high temperature and its optimal dielectric constant of around 20. It is used for metal coatings, as a refractory material in insulation, abrasives, enamels and glazes, as support material for catalysis and, due to its ion conductivity, it is also applied in gas sensors, oxygen pumps for partial pressure regulation and high temperature fuel cells. Further, ZrO<sub>2</sub> is one of the most radiation-resistant ceramics currently known and therefore has a particular importance in the nuclear industry [14]. In the present work, efforts have been made to the synthesis and characterization of surface modified cobalt with ZrO<sub>2</sub> ceramic particles, in order

to obtain a biocompatible material presenting at the same time good corrosion and wear performances. The composite materials were obtained by using dispersed micro sized ZrO<sub>2</sub> particles (mean diameter 10 μm) and cobalt plating electrolyte based on cobalt chloride. The major challenges with the co-deposition of second phase particles are the achievement of a high level of codeposition and avoiding the agglomeration of particles suspended in the electrolytes. However, in the literature, there are very limited studies in the dispersion of inert particles in the cobalt matrix and its influence on the overall properties.

It was used a bath solution without additive because it could give reactions with zirconium oxide (ZrO<sub>2</sub>) particles and the results could not have been interpreted properly. It is necessary to note that by involving the particles of zirconium oxide in a cobalt matrix we can obtain materials with properties differing from those of the individual materials.

## 2. Experimental Set-Up

For electrodeposition we used a cell shown in Fig 1. Cobalt plate of 99.9% purity was used as anode.



*Fig 1. Schematic electrochemical cell for electrodeposition*

As cathode we used 304L stainless steel plates whose chemical composition and mechanical properties are presented in Table 1. They degreased with alkaline solution, after being etched with HCl 10% for 1-2 min and washed with distilled water.

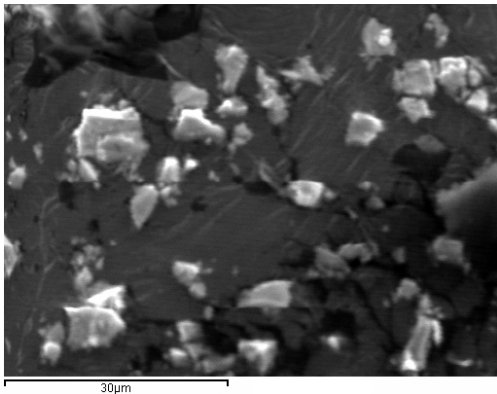
**Table 1. Chemical composition and mechanical properties for 304L stainless steel**

Steel	Chemical composition (%)									Yield strength N mm <sup>-2</sup>	Max tensile strength N mm <sup>-2</sup>	Min % total elongation 80 GL mm
	Cr	Mn	Si	P	S	Ni	Cu	Mo	Ti			
304	19,79	1,74	0,17	0,028	0,005	10,02	0,86	0,74	0,15	210-250	520-720	45

The ZrO<sub>2</sub>/Co composite coatings were obtained from a suspension of ZrO<sub>2</sub> particles in aqueous cobalt chloride electrolyte having the composition presented in Table 2.

**Table 2.** Composition and operating conditions for electrodepositing Co

CoSO <sub>4</sub> x 7 H <sub>2</sub> O	20 g/L
CoCl <sub>2</sub> x 6 H <sub>2</sub> O	300 g/L
H <sub>3</sub> BO <sub>3</sub>	30 g/L
Temperature	25°C
pH	3.5 – 4
Current density	45.7 – 5.7 mA/cm <sup>2</sup>
U	2 V
Time	30 min
Stirred	500 rpm



**Fig. 2.** SEM image of ZrO<sub>2</sub> particles

In the second phase dispersed of ZrO<sub>2</sub> were added to electrolyte at 20 g/L and stirred at 500 rpm 24 hours before electroplating. The shape and dimension of ZrO<sub>2</sub> particles are presented in Fig. 2 (SEM image). Cobalt chloride increases the conductivity and ability of uniform deposition and boric acid was used like buffering agent who stabilized the acidity of electrolyte.

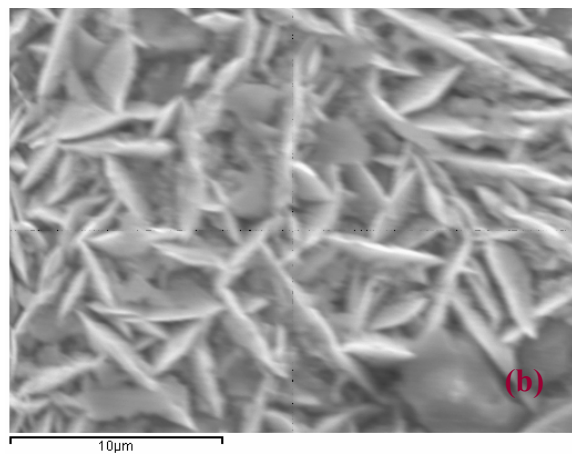
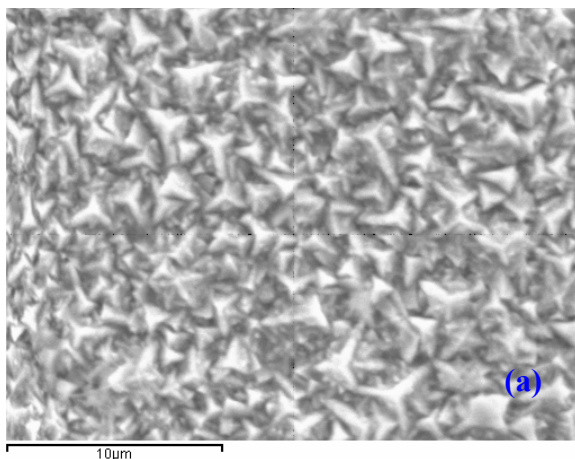
The morphology of deposits was examined by scanning electron microscopy SEM coupled with energy dispersive X-Ray analysis (EDX) on surface and cross section of samples. The coating thickness was examined by optical microscopy in cross section of samples as well as by weighting the cathode before and after deposition.

### 3. Results and discussions

Scanning electron microscopy micrographs of the deposits obtained at two current densities of 45.7 mA/cm<sup>2</sup> and 28.57 mA/cm<sup>2</sup> respectively are shown in Figs. 3-4.

The ZrO<sub>2</sub> particles appear sufficiently well distributed, compact and continuous. Nevertheless, the ZrO<sub>2</sub>/Co composite coatings obtained at same current densities as pure cobalt coatings have different shape and grain size than the pure cobalt.

Figure 3 compares a pure cobalt coating and ZrO<sub>2</sub>/Co composite coating obtained at 45.7 mA/cm<sup>2</sup> current density, 30 min deposition time and a stirring rate of 500 rpm (5000x magnification).



**Fig. 3.** SEM surface morphology of (a) pure cobalt and (b) ZrO<sub>2</sub>/Co composite coatings obtained at 45,7 mA/cm<sup>2</sup> (5000x)

Figures 4 compares ZrO<sub>2</sub>/Co composite coating obtained at 28.57 mA/cm<sup>2</sup> with pure cobalt coating at same current density, (5000x magnification).

The surface morphology of composite layers is different compared with pure cobalt coating. The pure

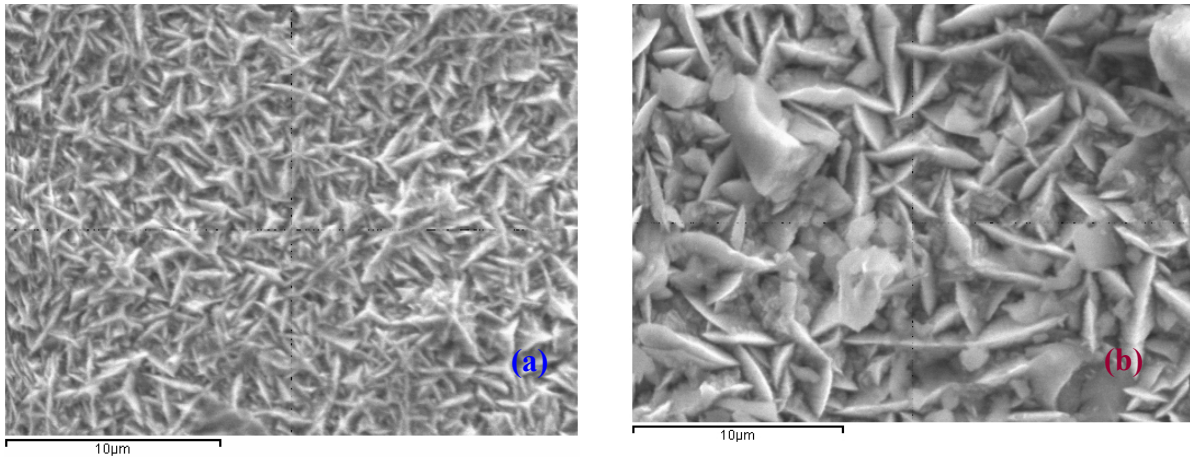
cobalt coating has a rather regular surface, whereas the composite coatings surface has disturbed surface structure.

By increasing the zirconium oxide particles concentration in the cobalt electrolyte the surface

structure of composite coating is changed more to finer crystallites. The zirconium oxide acts as disturbing the crystals size of electrodeposited cobalt during co-deposition. The zirconium oxide could have an inhibition effect of cobalt crystals growth and a catalytic effect in increasing nucleation sites.

Studying the zirconium oxide distribution in the cobalt matrix on cross sections of coatings, Figure 5 (a, b) by SEM image and EDX element distribution

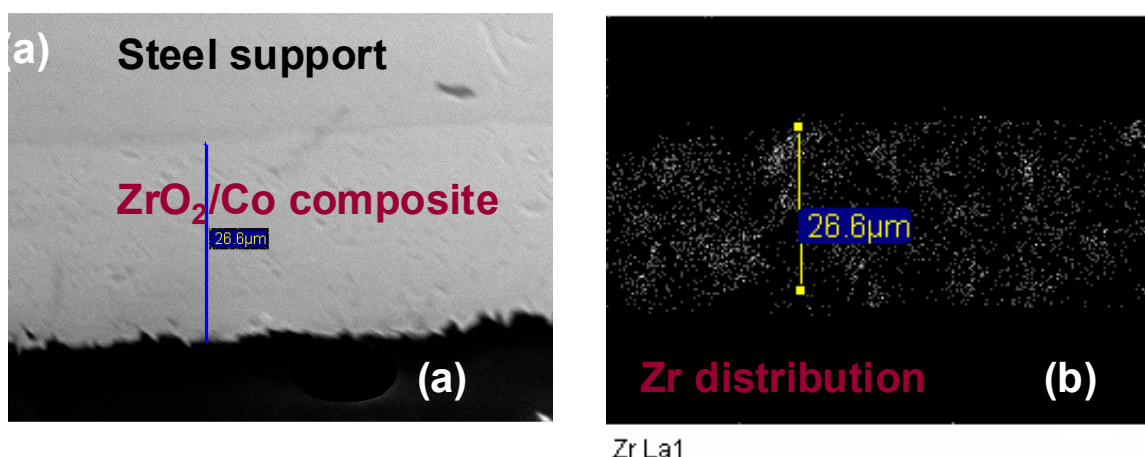
(Zr) shows a good dispersion phase inside cobalt and a good adhesion and uniformity for  $ZrO_2/Co$  composite coatings on stainless steel support. The SEM -EDX images of Co and  $ZrO_2/Co$  composite coatings, on stainless steel, show the presence of dispersed phase in the cobalt matrix, which is uniformly distributed. Also SEM shows the modification of surface morphologies of cobalt matrix by adding the  $ZrO_2$  dispersed particles.



**Fig. 4.** SEM surface morphology of (a) pure cobalt and (b)  $ZrO_2/Co$  composite coatings obtained at  $28,57\text{ mA/cm}^2$  (5000x)

The layers thickness of pure cobalt and  $ZrO_2/Co$  composite coating calculated by weighting the deposits are presented in the Figure 6. It shows an increasing of coating thickness with increasing of current density for both types of coatings. However the increasing of thickness of  $ZrO_2/Co$  composite is a

little bit higher compared with pure cobalt at the same current density. This could be explained by increasing the current efficiency of electroplating process in the presence of  $ZrO_2$  dispersed particles in chloride cobalt electrolyte.



**Fig. 5.** SEM image of  $ZrO_2/Co$  composite coatings in cross section showing the: (a) coating thickness and (b) uniform distribution of the zirconium oxide inside the cobalt matrix by EDX signal of zirconium in mapping mode

The coating thickness could be determined more accurately by optical microscopy in cross section,

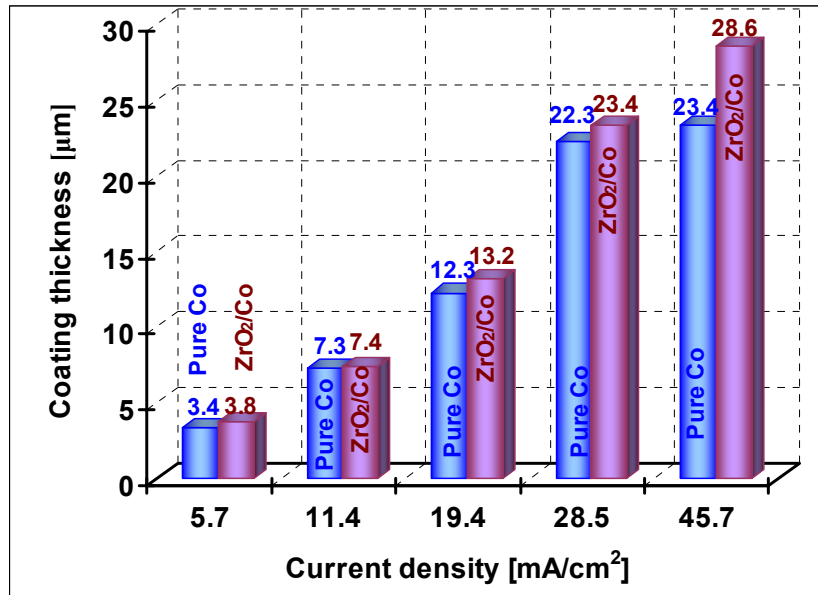
Figure 7. By studying the cross sections of  $ZrO_2/Co$  composite coatings it was observed also the good



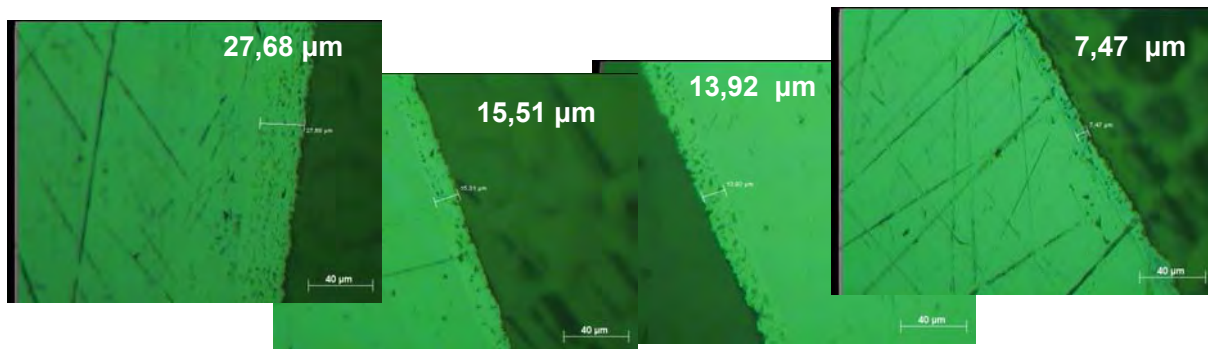
adhesion and uniformity. The amount of ZrO<sub>2</sub> dispersed phase inside the cobalt matrix for ZrO<sub>2</sub>/Co composite coatings was determined by zirconium analysis and transformed in zirconium oxide. By increasing the current densities of co-deposition process, the amount of ZrO<sub>2</sub> particles decreases in the

composite coatings as it is shown in the Figure 8.

The highest amount of ZrO<sub>2</sub> particles in the composite deposit was found at smallest current density of 5.7 mA/cm<sup>2</sup>, respectively. The smallest amount of second phase was co-deposited with cobalt at highest current density of 45.7 mA/cm<sup>2</sup>.



**Fig.6.** (■) Pure Co coatings thickness and (■) Co+ ZrO<sub>2</sub>/Co (20g/L ZrO<sub>2</sub> in the electrolyte) composite coating thickness versus current density at deposition time of 30 min.



**Fig.7.** Coating thickness of ZrO<sub>2</sub>/Co composite coatings measured in cross section by optical microscopy, the coatings were obtained at current density from 45,7 mA/cm<sup>2</sup> at 5,7 mA/cm<sup>2</sup> at constant time of electrodeposition

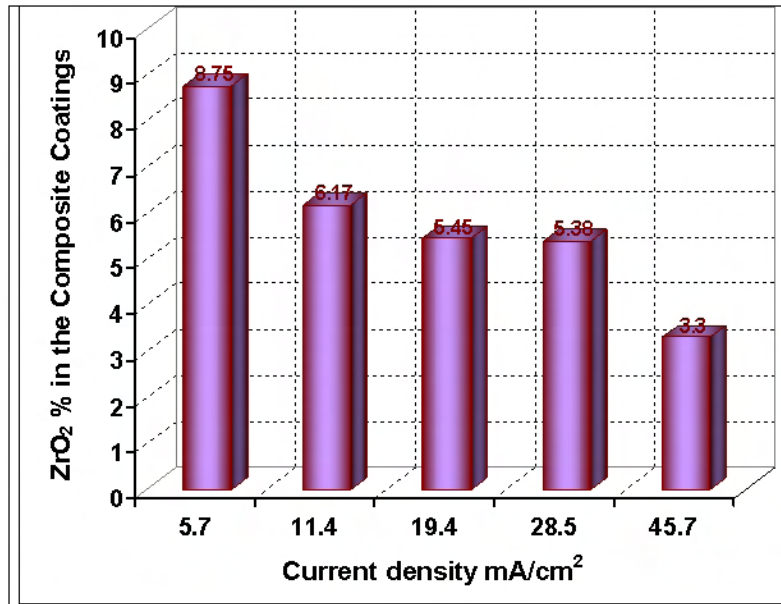
The data presented in Figs. 6 and 8 suggest that ZrO<sub>2</sub>/Co films can only be deposited at low current densities (< 11 mA/cm<sup>2</sup>) in order to have the highest amount of ZrO<sub>2</sub> codeposited under the deposition conditions applied in the present study.

The dependence of composition on applied current density is illustrated in Fig. 8. ZrO<sub>2</sub> content in the film decreases from about 9 to 3 wt.% when the current density is increased from 5.7 to 45.7 mA/cm<sup>2</sup>.

The easy occurrence of preferred orientation in electrodeposited cobalt has stimulated number of investigations, without however, achieving the stage of a comprehensive view [16]. Cobalt electrocrystallisation has been far less studied compared to Ni. Electrolytic Co crystallizes with both hexagonal closed packed (hcp, α-Co) the stable allotropic modification at temperature below 417<sup>o</sup>C and face centered cubic (fcc, β-Co) lattice structure,

as first reported by Hull [16].  $\beta$ -Co is favored by low temperature, high current density and low pH. With the increase of pH the structure becomes complete of the  $\alpha$ -phase and deposits texture depends mainly on solution pH and, to a minor extent, on temperature and current density. Our results regarding Co and

ZrO<sub>2</sub>/Co composite electrodeposition from chloride electrolyte seem to have a two-phase composition and need more inside investigation in order to explain the changes in surface morphology of composite coatings as compared with pure cobalt layers obtained in the same electroplating conditions.



*Fig.8. Content of the ZrO<sub>2</sub> dispersed phase inside the ZrO<sub>2</sub>/Co composite coatings versus current density*

Advances in the comprehension of the factors and mechanism participating in Co electro crystallization are expected to contribute to a systematic understanding of the structure-properties correlation of cobalt and matrix cobalt composites.

#### 4. Conclusions

It is feasible to prepare ZrO<sub>2</sub>/Co composite coating by properly incorporating the ZrO<sub>2</sub> microparticulates to be co-deposited in the Co plating bath from a chloride cobalt solution.

Coatings thickness increases with increasing current density; the composite layer is almost equal or a little bit higher to that of the cobalt matrix at same current density.

Moreover, the incorporation of the ZrO<sub>2</sub> microparticulates in the plating bath leads to changes in the morphology of the composite coatings as compared to the pure Co coatings evidenced by SEM studies.

The surface morphology of composite coatings layers is different compared with pure cobalt coated. The regular crystal structure characteristic of electroplated cobalt coatings was distributed by ZrO<sub>2</sub> particles in cobalt electrolyte for electrodeposition.

We obtained a very good distribution of ZrO<sub>2</sub> particles on cobalt surface.

The amount of zirconium oxide embedded in the cobalt matrix decreases with the increasing of the current densities of electroplating process.

The adhesion and uniformity of ZrO<sub>2</sub>/Co composite coatings were analyzed by SEM and optical microscopy showing good results.

The future work will be done on the following directions: modelling the mechanism of co-deposition and electroplating parameters; correlation of coating thickness with electrodeposition parameters. The mechanical behavior of the modified materials is still investigated by scratch and pin-on-disc wear tests; Electrochemical Corrosion in Simulating Body Fluids (SBF); tribocorrosion studies in SBF; biocompatibility tests; bacteria attachment and biofilm growth.

#### Acknowledgments

The authors gratefully acknowledge the International Cooperation Project Bilateral Romania-France Programme Humbert Curien (PHC) – Brancusi: *Etude de dépôts composites nanostructurées pour surfaces fonctionnelles*, number 19603 PC.



## References

- [1]. **Karl U. Kainer** - *Metal matrix composite*, Publisher Wiley, 2006
- [2]. **T.W.Clyne, P.J.Withers** - *An Introduction to Metal Matrix Composites*, Cambridge University Press, Cambridge, 1993
- [3]. **L.Benea, P.L.Bonora, A.Borello and S.Martelli** - *Wear* **249** (2002), pp 994-1003
- [4]. **L.Benea, P.L.Bonora, A.Borello and S.Martelli** - *Materials and Corrosion*, **53** (2002), pp.23-29
- [5]. **T.L. Yau** - *Stress-corrosion cracking of zirconium alloys*, in: R.H. Jones (Ed.), *Stress-Corrosion Cracking: Materials Performance and Evaluation*, ASM International, Materials Park, OH, 1992
- [6]. **A. Heuer, L.W. Hobbs (Eds.)** - *Science and Technology of Zirconia*, *Advances in Ceramics*, vol. 3, American Ceramic Society, Westerville, OH, 1981; *Science and Technology of Zirconia II*, *Advances in Ceramics*, vol. 12, American Ceramic Society, Westerville, OH, 1984.
- [7]. **S. Somiya, N. Yamamoto, H. Yanagina (Eds.)** - *Advances in Ceramics*, vols. 24A and 24B, American Ceramic Society, Westerville, OH, 1988.
- [8]. **X. Zhao, D. Vanderbilt** - *Phys. Rev. B* **65** (2002) 075105.
- [9]. **E.J. Walter, S.P. Lewis, A.M. Rappe**, *Surf. Sci.* **495** (2001) 44.
- [10]. **A. Meldrum, L.A. Boatner, R.C. Ewing** - *Phys. Rev. Lett.* **88** (2002).
- [11]. **C. Morant, J.M. Sanz, L. Gal'an** - *Phys. Rev. B* **45** (1992).
- [12]. **V. Fiorentini, G. Gulleri**, *Phys. Rev. Lett.* **89** (2002).
- [13]. **R. Punthenvilakam, E.A. Carter, J.P. Chang** - *Phys. Rev. B* **69** (2004)
- [14]. **D. Hudson, A.Cerezo, G.D.W.Smith**, *Ultramicroscopy* (2008)
- [15]. **F. Bratu, L. Benea, J.P. Jean-Pierre Celis** *Surf Coat. Technol* **201**(16-17), 2007, pp. 6940.
- [16]. **A. Vicenzo, P.L. Cavallotti**; *Electrochim. Acta* **49** (2004) 4079-4089.