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Ni-P COATING ON STEEL SUPPORT BY ELECTROLESS METHOD

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ABSTRACT

The autocatalytic reduction method (electroless method) was applied to obtain the Ni-P layers with different P contents. Nickel sulfate was used as nickel ion source and as reducing agent the sodium hypophosphite. The surface morphology, microstructure, layers thickness and corrosion resistance in acidic and basic environment were analyzed. The research results show a strong connection between layer characteristics and process parameters: pH and temperature. The analyzed layers show a high stability in 10% NaOH solution and different corrosion rates in HCl solutions (1 N and 0.5 N) depending on the phosphorus content in the layer.

KEYWORDS: Ni-P alloys, macrostructure, microstructure, corrosion resistance

1. Introduction

The electroless deposition method consists of the immersion of the support in a solution containing, in principle, a salt for providing the ions of the metal to be deposited and a reducing agent. Several metals and alloys can be deposited through this method, such as: Sn, Cu, Mn, Co, Ni-P, Ni-B, Ni-P-Sn, Ni-P-Zn: and others, on different supports: steel, Al, Mg, Cu, *et all*. The name of the method comes from the fact that no external electrical source is used. When Ni-P alloys layers are obtained, the solution contains $NiSO_4$ or NiCl and the reduction is done with sodium hypophosphite. By using hypophosphite ions as a reducing agent, the reactions underlying the deposition of Ni-P on the active surface of the support are the following [1]:

$$Ni^{2+} + H_2PO_2^- + H_2O \rightarrow Ni + 2H^+ + H\left(HPO_3\right)^- \quad (1)$$

$$HPO_2^- + H_2O \rightarrow H\left(HPO_3\right)^- + 1/2H_2 \quad (2)$$

When using sodium hypophosphite, Ni-P coatings with phosphorus in varying concentrations are obtained, from 1 to 12%, depending on the process parameters. The phosphorus content is very important as it determines the structure and consequently the properties of the coating [2-4]. Ni-P layers with low-phosphorus have a high resistance to wear that can be improved by heat treatment [5-7]. High P content in the layer grants high corrosion resistance [8-10]. The method also has the advantage of covering supports with complicated configurations because the deposited layer closely follows the topography of the surface [11].

Many of the reactions from the electroless process are sensitive to the changes in the solution pH. The main nickel reduction reaction is accelerated by the increase of the pH and, since it predominantly controls the deposition rate, increasing the pH of the solution leads to an increase in the nickel deposition rate. At the same time, the increase of the solution pH leads to a slowdown in phosphorus reduction due to the production of hydroxide ions. Therefore, increasing the solution pH leads to decreases in the phosphorus content of the coating. To maintain the pH at the desired values in the coating solution, a buffering agent is inserted. Specialty literature indicates a wide range of such substances [12]. The solution may also contain other additives that improve the stability and the characteristics of the deposited layer [13]. This paper shows the way to obtain Ni-P alloy layers, with different phosphorus content, by electroless method using a simple and accessible solution that can also be applied industrially.

2. Experimental conditions

The bath used to obtain Ni-P layers contains the following salts:

- nickel sulphate, as a supplier of nickel ions - 25 g/L;
- sodium hypophosphite, as reducing agent - 23 g/L;
- sodium acetate, as complexing and buffering agent - 9 g/L;
- lead acetate, as a stabilizer by lead ions - 0.01 g/L.

The salts were dissolved in distilled water and placed in the bath of the experimental installation, charged with 0.5 L distilled water at 70 °C, in the following order: lead acetate, sodium acetate, nickel sulfate and sodium hypophosphite.

After the salts were introduced, the bath was filled with distilled water up to the work volume (1 L) and the solution was stirred at 300 rpm. The working temperature was 83 °C and pH 6.6; 5.11 and 4.32. The pH was corrected with glacial acetic acid or ammonium hydroxide, as appropriate. The cleaning of the surface of steel strips samples had three operations:

- cleaning in commercial solution (MASCO) at pH = 2 and 60 °C; immersion time 3 min;
- washing in hot water at 60 °C;
- washing in hot water at 80 °C.

3. Characterization of layers

For the characterization of the samples, specific analyses were made to determine the main characteristics of practical interest, namely:

- chemical and structural analysis;
- layer thickness;
- corrosion behavior.

3.1. Chemical composition

The chemical composition was determined by EDX analysis on an electron microscope, Quanta 200 type, equipped with an X-ray analyzer. The analysis was performed in layers section, obtained at the three experimental pH values (4.3, 5.11, 6.6) at a 5 minutes immersion time, at 83 °C. EDX spectra show an increase of phosphorus content to at lower pH. Figure 1 shows the result of EDX analysis on a Ni-P layer obtained at pH = 5.11. The diffraction spectrum presents, alongside Ni and P, peaks for Fe, C and O. Fe and C come from the steel support and O occurs as a result of surface oxidation. The chemical analysis showed phosphorus contents from 4.74 (pH = 6.6) to 12.42 wt.% (pH = 4.3). At pH = 5.11 the phosphorus contents were 9.53 wt.%.

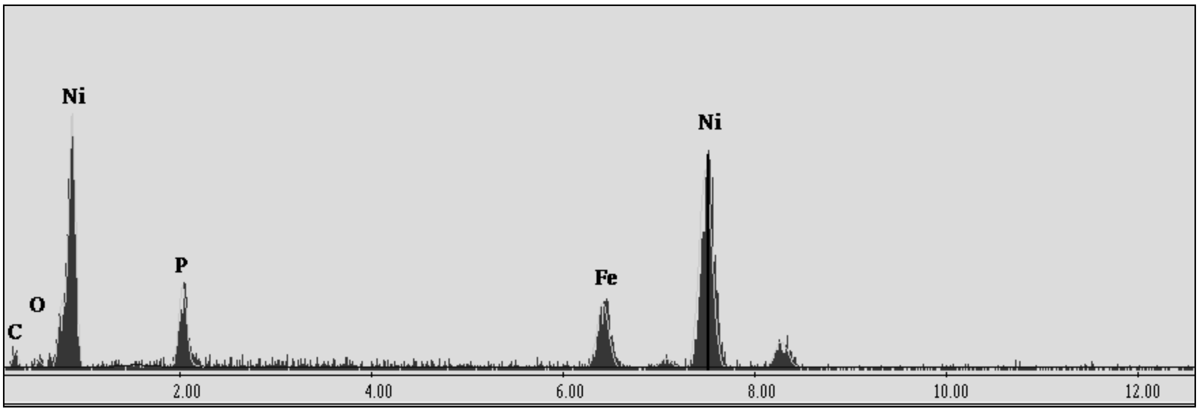


***Fig. 1.** EDS spectra for the Ni-P layers obtained at pH = 5.11 and 5 min immersion time, at 83 °C*

3.2. Surface morphology

The macroscopic surface of the Ni-P coated strips has a very glossy and smooth silvery look. Microscopically (Fig. 2, a, b, c), regardless of the experimental conditions, a strip deposit is observed which closely follows the roughness of the steel substrates. Moreover, an increase in the layer’s uniformity is observed, at decreasing the pH, without having the substrate roughness completely disappear. (Fig. 2c).

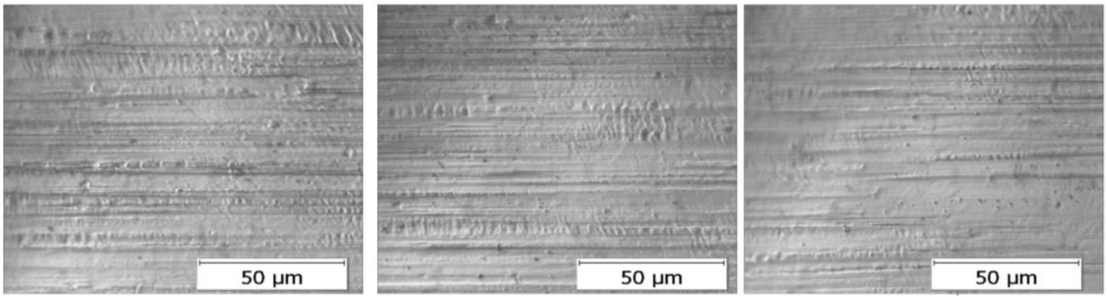
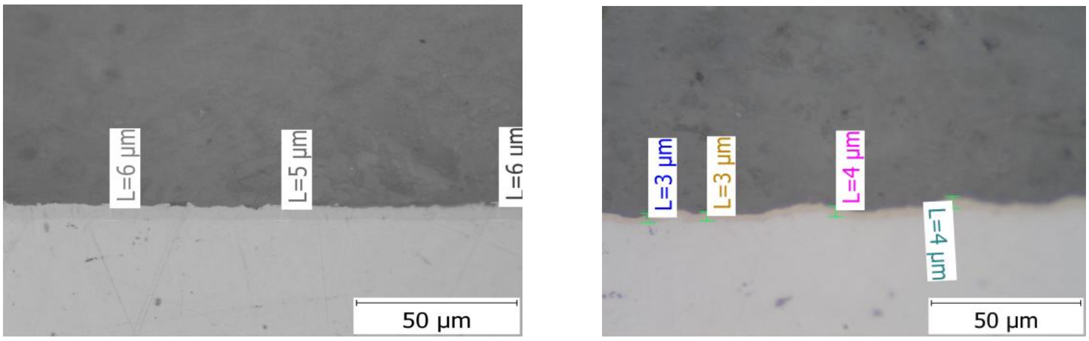


Fig. 2. *Optical micrographs of Ni-P layer depending on the pH, T = 83 °C, 5 min.*

3.3. Layer thickness

The layer thickness is a challenge in the electroless coating method. The deposition is relatively slow and, only when the optimum parameters are assured, a thickness over 20 µm can be obtained. Out of these parameters, the immersion time is important but also the temperature and pH. In order to ensure high productivity, the nickel-plating process requires a reduced duration, a high working temperature and an acidic pH. In order to analyze the effect of the considered working parameters on the thickness of the layer, the metallographic measurement method was applied. In Figure 3 a, b the optical thicknesses are presented, measured on the optical microscope, which were obtained at immersion times of 5 minutes at 83 °C at the three experimental pHs. There is a decrease in layer thickness from 5 µm to 2 µm, when the pH decreases.

For the electroless process, the nickel deposition rate increases exponentially at temperature rise, the variation curve being similar to other deposition techniques (Fig. 4).



a) pH-6.6 b) pH-4.32

Fig. 3. *Influence of the pH on layer thickness*

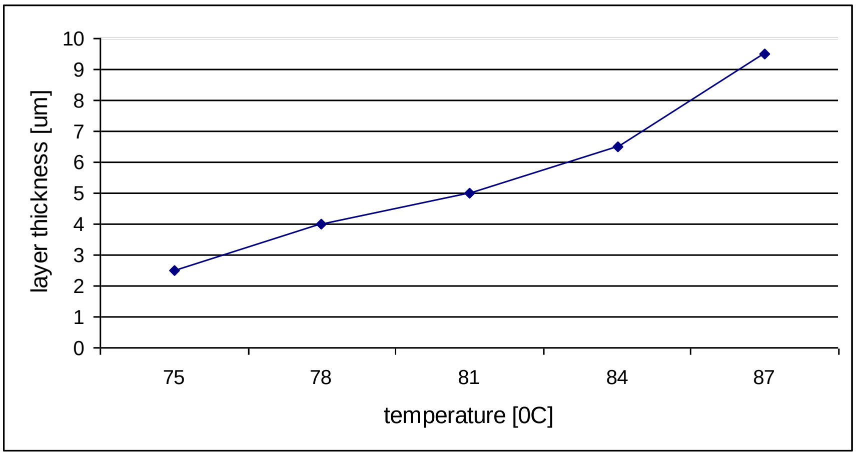


Fig. 4. *Influence of the temperature on layer thickness*

The deposition rate is low at temperatures below 75 °C and increases with temperature increase [14]. Generally, in the nickel electroless process the maximum working temperature is about 90 °C. Above this temperature the bath tends to become unstable.

3.4. Corrosion resistance

The corrosion resistance evaluation was done in various corrosive environments by gravimetric method, according to G1 / 2004.

The following steps were taken:

- weighing with four decimals of the samples, resulting in the initial mass;
- immersion in crystallizers, where the corrosive environment is;
- removing samples after a determined time and washing them with distilled water to remove corrosion products and then with acetone followed by drying;
- weighing dry samples.

Samples were selected with different phosphorus contents (small, medium, high) obtained at different pH values coded according to Table 1.

Table 1. *Samples tested*

Code	Layer types and conditions of obtaining
NP1	layer Ni-P with small phosphorus (4.47 wt.% P), obtained at pH-6.60, 83 °C, 5 min.
NP2	layer Ni-P with medium phosphorus (9.53 wt.% P), obtained at: pH-5.11, 83 °C, 5 min.
NP3	layer Ni-P with high phosphorus (12.42 wt.% P), obtained at: pH-4.32, 83 °C, 5 min.

These samples were individually submerged, according to G31 / 2004, in containers containing 1 N and 0.5 N hydrochloric acid solution. Samples were weighed to determine the initial mass and measured for surface determination.

The study was conducted over a period of 168 hours (one week) For the calculation of the corrosion rate, the following relation was applied:

$$v_{cor} = \frac{m_{cor}}{S \cdot t}$$

where:

v_{cor} - gravimetric index [g/m^2·h];
m_{cor} - mass loss by corrosion [g];
S - surface area of the samples [m^2];
t - corrosion time [h].

3.4.1. Corrosion behavior estimation, in corrosive environment 1 N HCl

For each type of layer, the corrosion rate in 1 N hydrochloric acid was determined as average on samples subjected to corrosion (minimum three per coating type). The results after 168 hours are presented in Figure 5. As it can be seen from this data, the sample with a medium phosphorus content (Vcor = 1.35) has the best corrosion behavior in this highly corrosive medium and the sample with lower phosphorus content (Vcor = 2.60) the weakest behavior.

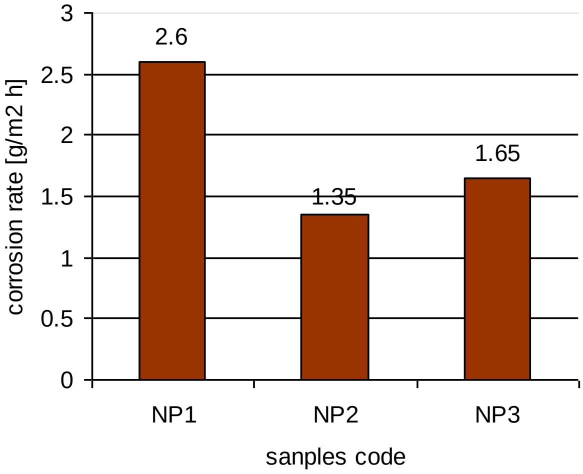
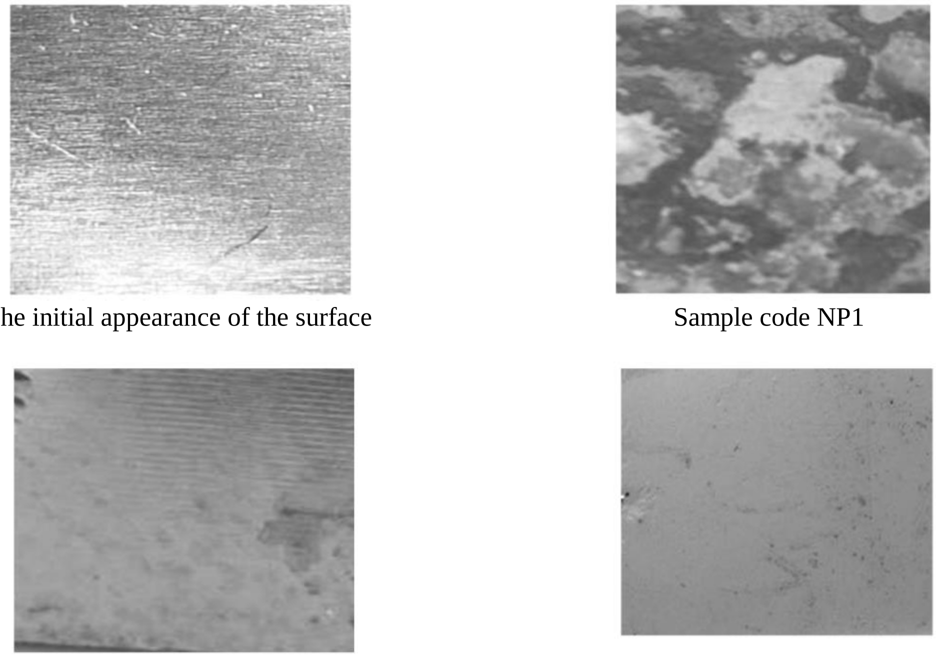


Fig. 5. *Corrosion rate in 1 N HCl depending on the type of protection layer, after 168 hours of testing*

The direct observation of the samples, after 168 hours of corrosive attack, showed an attenuation of the metallic gloss for all samples. Moreover, on all samples were localized attacks with the formation of red rust spots. Figure 6 shows aspects of the surface of highly corroded samples.

Localized corrosion is specific to nickel coatings because it provides a cathodic protection to the steel support, so any porosity or nonuniformity of the layer will result in a strong corrosive effect of the steel substrate. The localized corrosive attacks observed on samples may also be caused by microscopic defects such as micro-porosity or discontinuity of the layer due to the presence of impurities anchored from the nickel bath as shown in Figure 7.


The initial appearance of the surface

Sample code NP1

Sample code NP2

Sample code NP3

Fig. 6. *Macroscopic appearance of Ni-P layers after corrosive attack in 1 N HCl solution, 1:1*

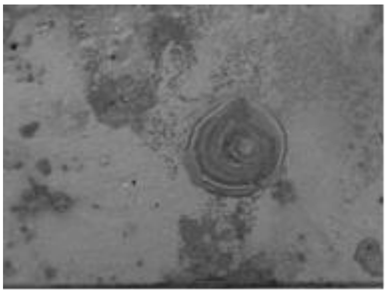


Fig. 7. *Localized corrosion caused by a pore, 1:1*

3.4.2. Corrosion behavior in corrosive environment 0.5 N HCl

The results of the corrosion process after 168 hours in 0.5 N HCl are shown in Figure 8. The sample with high phosphorus content (Vcor = 0.43) has the best corrosion behavior in this corrosive environment and the sample with medium phosphorus content (Vcor = 2.64) has the highest corrosion rate.

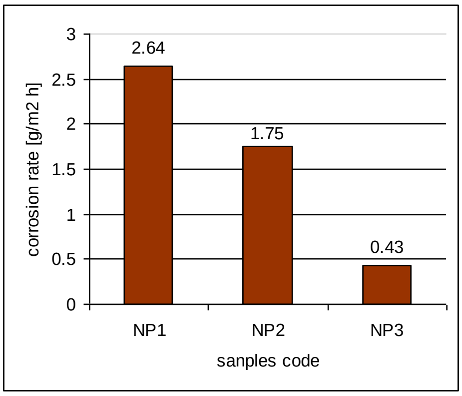


Fig. 8. *Corrosion rate in 0.5 N HCl depending on the type of protection layer, after 168 hours of testing*

Macroscopic analysis (with the naked eye and magnifying glass X20) shows the production of generalized corrosion, with the formation of a smaller amount of corrosion products than the previous test.

3.4.3. Assessment of corrosion resistance in the basic environment

The basic environment in which the samples were individually immersed was 10% NaOH solution. They were kept for 1.512 hours, every 168 hours being removed, washed, dried and weighed. As it can be seen in Table 4, mass loss is zero or within the range of 0.0001-0.0003 (within the error limit), which means zero corrosion rate in 10% NaOH. All types of coatings tested proved to be practically inert in the alkaline medium during the experiment.

Table 4. *Test results in 10% NaOH solution*

Sample mass	NP1	NP2	NP3
m_0 (initial)	0.7866	1.3432	3.9313
m_1 (after168 hours)	0.7866	1.3434	3.9315
m_2 (after 336 hours)	0.7867	1.3433	3.9314
m_3 (after 504 hours)	0.7866	1.3432	3.9315
m_4 (after 672 hours)	0.7866	1.3433	3.9313
m_5 (after 840 hours)	0.7865	1.3433	3.9314
m_6 (after 1008 hours)	0.7868	1.3437	3.9313
m_7 (after 1176 hours)	0.7864	1.3433	3.9314
m_8 (after 1344 hours)	0.7865	1.3436	3.9316
m_9 (after 1512 hours)	0.7868	1.3433	3.9313

4. Conclusions

Ni-P alloy layers with different phosphorus content obtained by electroless method used a simple and approachable solution: nickel sulfate 25 g/L, sodium hypophosphite 23 g/L, lead acetate 0.01 g/L and sodium acetate 9 g/L.

The surface of the Ni-P layers obtained has a very glossy and smooth silver look with an increase of the uniformity at pH decrease.

It is observed a decrease in layer thickness from 5 µm to 2 µm when the pH decreased from 6.6 to 4.32;

The sample with 9.53 phosphorus content (Vcor = 1.35) has the best corrosion behavior in 1 N hydrochloric acid (after 168 hours of testing) and the sample with 4.47 phosphorus content (Vcor = 2.60) has the weakest corrosion behavior.

All types of coatings tested proved to be practically inert in the alkaline medium during the experiment (1512 hours).

References

[1]. Krishnan K. H., John S., Srinivasan K. N., Praveen J., Ganesan M., Kavimani P. M., *An Overall Aspect of Electroless Ni-P Depositions - A Review Article*, Metallurgical and Materials Transactions A, vol. 37A, June 2006.

[2]. ***, *Quality Metal Finishing guide. Electroless Nickel Plating*, vol. 1, no. 5, http://infohouse.p2ric.org/ref/25/24301.pdf.

[3]. Mallory O. G., Hajdu J. B., *Electroless Plating: Fundamentals and Applications*, sponsored and published by American Electroplaters and Surface Finishers Society, 1990.

[4]. Khim Myo, *Effects of surfactants on characteristics and applications of electroless nickel-phosphorous deposits*, chapter 2 of thesis master of engineering, 2003.

[5]. Balint S. I., Constantinescu S., Balint L., *Influence of heat treatment on the characteristics of Ni-P-Al_2O_3 composite layers*, 15th International Multidisciplinary Scientific GeoConference SGEM 2015, Conference Proceedings, book 6, vol. 1, p. 99-111, 2015.

[6]. Balint L., Ciocan A., Balint S. I., Alexandru P., *The effect of heat treatment on the structure and characteristics of electroless Ni-P layer*, 16th International Multidisciplinary Scientific GeoConference, SGEM 2016, Albena, Bulgaria, Conference Proceedings, book 6, vol. 1, p. 345-352, 2016.

[7]. Lucica Balint, Gina Genoveva Istrate, *Caracterisation Ni-P and composite Ni-P-Al_2O_3 electroless layers*, Proceeding UGALMAT 2016.

[8]. Gina Genoveva Istrate, Tamara Radu, *Corrosion Behavior of Ni-P Coated Steel Strips*, The Annals of “Dunarea de Jos” University of Galati. fascicle IX. Metallurgy and Materials Science. no. 3, p. 48-52, 2015.

[9]. Radu T., Vlad M., Potecasu F., Istrate G. G., *Preparation and characterisation of electroless Ni-P-Al_2O_3 nanocomposite coatings*, Digest Journal of Nanomaterials and Biostructures, vol. 10, no. 3, p. 1055-1065, 2015.

[10]. Sankara Narayanan T. S. N., Baskaran I., Krishnaveni K., Parthiban S., *Deposition of electroless Ni-P graded coatings and evaluation of their corrosion resistance*, Surface & Coatings Technology 200, p. 3438-3445, 2006.

[11]. Florentina Potecasu, Tamara Radu, *The Influence of the Steel's Surface Quality on the Electroless Ni-P Coatings*, The

Annals of “Dunarea de Jos” University of Galati. fascicle IX. Metallurgy and Materials Science, no. 1, p. 49-53, 2015.

[12]. Bielinski J., *The Role of Buffers and Coin Electroless Nickel Plating*, Oberflache Surface, vol 25, no. 12, p. 423-429, 1984.

[13]. Hari Krishnan K., John S., Srinivasan K. N., Praveen J., Ganesan M., Kavimani P. M., *An Overall Aspect of Electroless Ni-P Depositions-A Review Article*, Metallurgical and Materials Transactions A, volume 37A, p. 1917-1925, june 2006.

[14]. Istrate G. G., Balint S. I., Ciocan A., Dragan V., *Influence of technological parameters on layer thickness to obtain Ni-P electrolles coatings*,15th International Multidisciplinary Scientific GeoConference SGEM 2015, www.sgem.org, SGEM2015 Conference Proceedings, ISBN 978-619-7105-42-1 / ISSN 1314-2704, book 6, vol. 1, p. 113-125, June 18-24, 2015.