COMPARISON BETWEEN ECO-PROFILES OF INNOVATIVE PA-CVD AND TRADITIONAL GALVANIC COATINGS

B. DeBenedetti, S. Grassini, L. Maffia
Dipartimento di Scienza dei Materiali ed Ingegneria Chimica, Politecnico di Torino, Italy
bruno.debenedetti@polito.it

Introduction

The Life Cycle Assessment (LCA) for materials/process/product design is a convenient tool if the evaluation of different protective treatments of metals is conducted following a correct choice of the functional unit. This methodology may be used to supply management strategies with particular attention to the choice between alternative processes [1] and, in this work, it has been applied to SiO_x-like films deposited by PA-CVD process using as reference for the comparison the standard galvanic Ni/Cr-based coatings.

Objective

The need of alternatives to Cr^{VI} applications is a must for the well-known reasons, then new coatings for corrosion protection with multifunctional properties are necessary. The purpose of the MATECO European Project (Contract n° 505928-1) is to evaluate the possible use of the PA-CVD process, taking into account the up-mentioned need of the replacement of the hazardous protective coatings nowadays employed with ecological and economical alternatives. This study presents the preliminary activities carried out in such context.

The reference system, the **nickel plating process**, is used extensively as basis for engineering, electroforming and decorative purposes, with the objective to improve surface finish, corrosion resistance and wear resistance following to a further deposition of **Chromium** or other types of layers. Such layers are very thin, usually not exceeding an average thickness of 1,25 µm and can be obtained by galvanic deposition or PVD.

The alternative system, the **PA-CVD (*Plasma Assisted Chemical Vapour Deposition*)**, has the purpose of processing a wide variety of materials in order to improve their resistance to wear and to corrosion. This functionality is obtained by depositing SiO_x single-multi layer films (0,01-5 µm) characterized by high chemical and thermal stability and by low gas permeability. Starting from organo-silicon monomers, coatings are produced by means of not-equilibrium plasma source in a low-pressure chamber maintained at room temperature [2, 3].

System boundaries and functional unit

According to ISO 14040, the system boundaries determine which unit processes have been included within the LCA study [4]. Figures 1 and 2 show the system boundaries of galvanic and PA-CVD processes respectively.

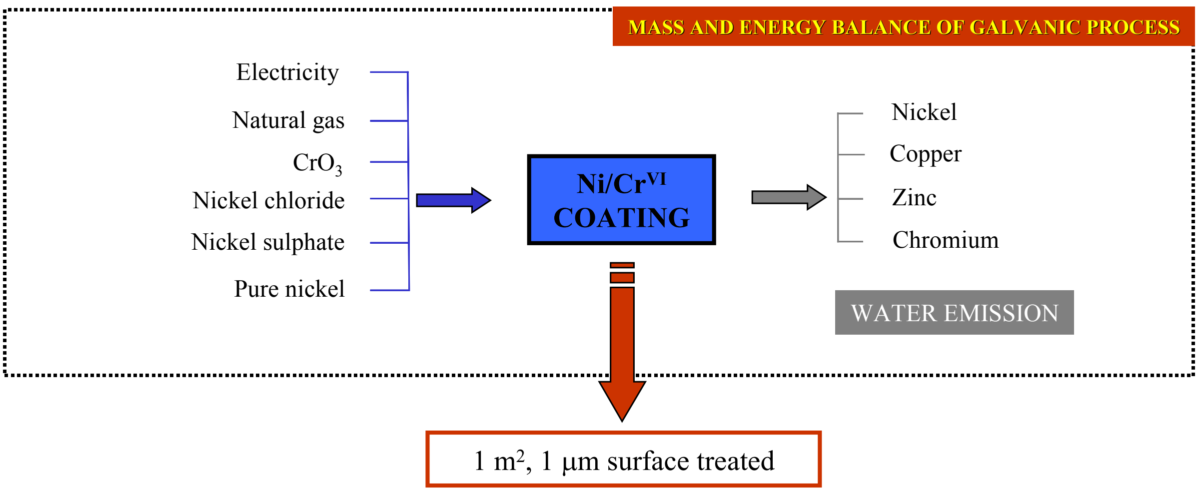

Fig. 1 – System boundaries of galvanic Ni/Cr technology

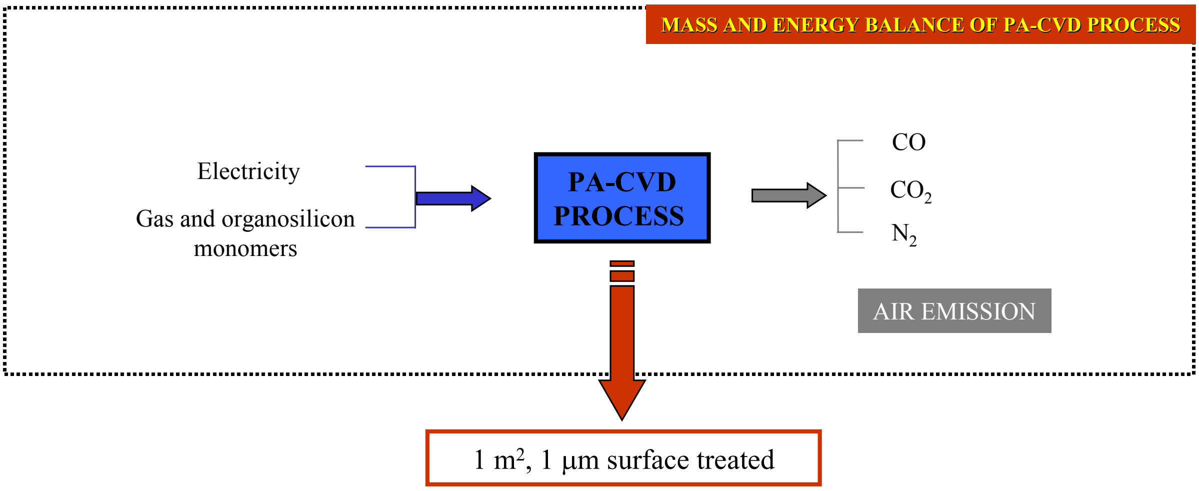

Fig. 2 – System boundaries of PA-CVD technology

The functional unit is a measure of the performance of the functional outputs of the product systems and its primary purpose is to provide a reference to which inputs, outputs and results are related [4]. As shown in the up reported figures, the easiest functional unit of the systems analysed is to consider a 1 m^2 surface protected by 1 micron of reported layer.
It is particularly important to underline that a further refinement of the functional unit is necessary as recently proposed in another case [5], because it is advisable to make the LCA analysis taking into account not only geometric characteristics of the coated system but also the layer properties as hardness, wear resistance and, especially, corrosion resistance. In particular it was proposed the adoption of a correction factor given by the ratio of the measured corrosion resistance of the examined process divided by the corresponding resistance of the reference process, in which, possibly, quick corrosion resistance measures as salt spray tests have been adopted.
Since the LCA activity in MATECO project has not been completed, at the moment the results of the salt spray tests are not available and the corrosion protective properties of PA-CVD coatings have been evaluated only on the basis of the results of electrochemical impedance measurements. The follow up of the present analysis will be carried out using a functional unit in which corrosion characteristics will be also taken into account.
The Boustead v.5 software was used as calculation model and as main source of secondary data; the here reported results refer to an average EU energy mix.

Results
As usual, the results of the LCA are splitted into the following categories: **energy results**, represented by GER (*Gross Energy Requirements*) indicator, that characterize the energy consumption for each functional unit, and **environmental results**, concerning natural resources consumption, air emissions, water emissions and solid wastes for each functional unit.
In this paper, the above-mentioned environmental results will be not explicitly reported; however, according to ISO 14042, they will be converted into environmental indicators by means of several standardised mandatory elements. For this analysis the following impact categories are considered: Greenhouse effect (GWP_{100} - Global Warming Potential) and Acidification (AP - Acidification Potential).
Figure 3 presents the results obtained in a lab-scale PA-CVD plant using for each indicator a conventional value (galvanic coating = 100).

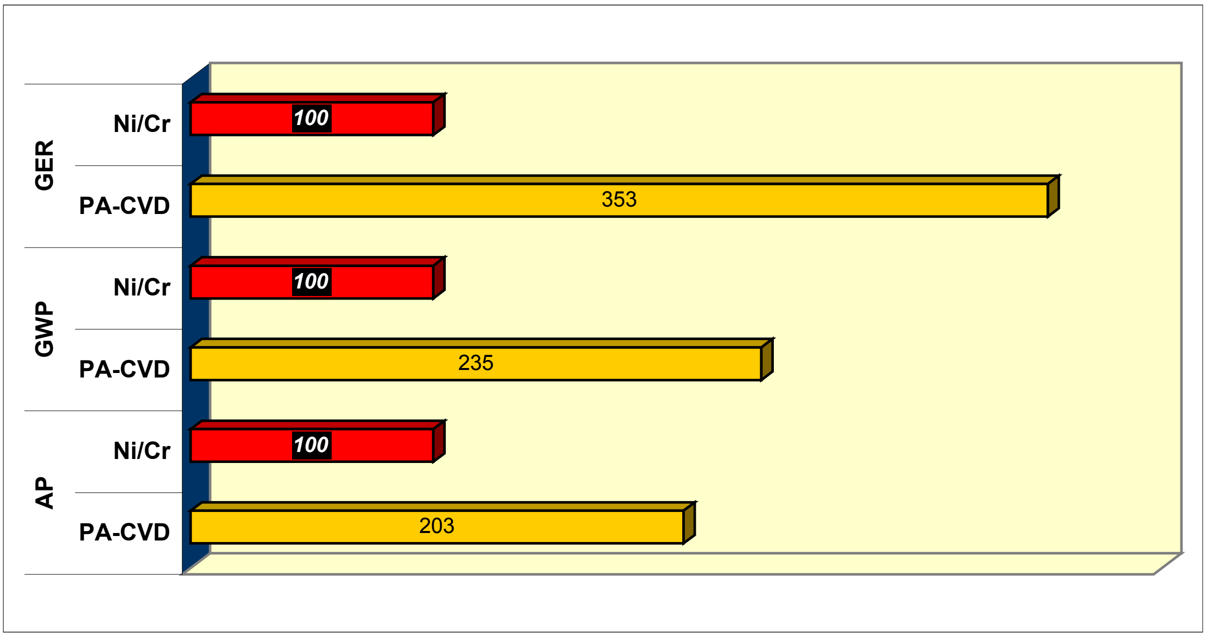

Fig. 3 – LCA results (Ni/Cr process = 100)

From an energy consumption viewpoint, the Ni/Cr coatings require a lower quantity of direct process energy with respect to the PA-CVD process and this is especially relevant for the electricity consumption (Figure 5).
The Energy mix to produce electricity is therefore relevant to define the environmental burden of the two systems. In particular, in the case of PA-CVD, the use of renewable electricity sources (as photovoltaic systems) and the increase of the process efficiency could be a good way to improve the environmental performances.
Considering the indirect contribution, the production of Cr, Ni is the most important feature of the galvanic system, even if such values are substantially negligible (Figure 4).
Moreover, the higher use of electricity of the PA-CVD process is balanced by higher direct solid, air emission and generation of exhaust solution of the Ni/Cr process. This means that from a local environmental point of view, the PA-CVD process avoid the direct emissions of metals (Ni, Cr, Zn and Cu in particular) but it generates an indirect contribute from the power plant. But the main environmental problem is that the layer of chromium applied over the nickel coating is obtained starting from CrO_3: such compound is a source of hexavalent chromium (Cr^{VI}), hazardous substance prohibited by EU legislation starting from 2007.

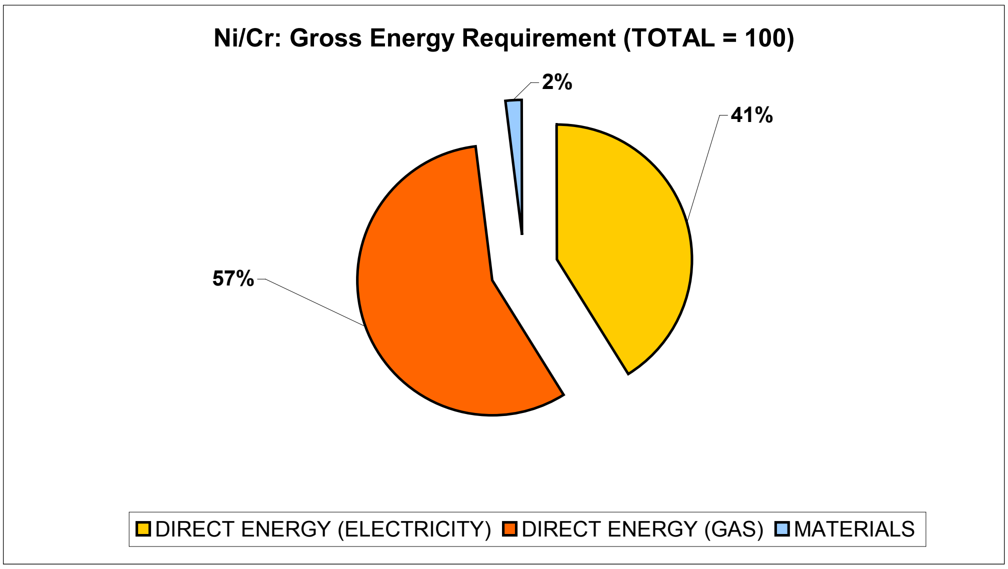

Fig. 4 – Contributes of energy and materials to GER for Ni/Cr technology

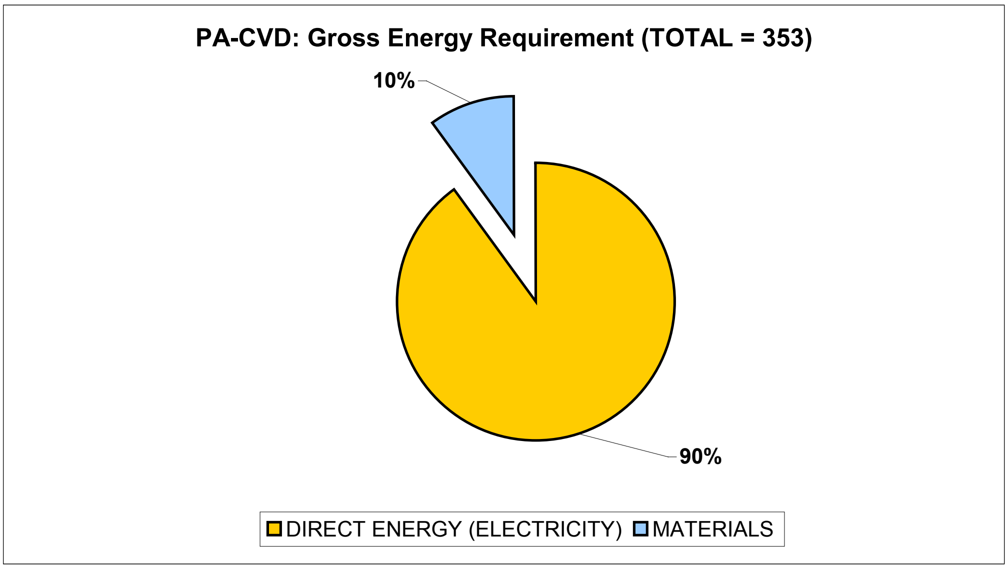

Fig. 5 – Contributes of energy and materials to GER for PA-CVD process

Even though Ni/Cr coatings exhibit good corrosion properties [6, 7], steel and magnesium alloys substrates coated with SiO_2-*like* film are characterised by impedance values ranging from $1{\cdot}10^5$ to $1{\cdot}10^7$ $\Omega{\cdot}cm^2$ in chloride-containing environments [8, 9].

Conclusions

From the evaluation of the main global environmental impact indicators, it can be observed that the PA-CVD involves high Gross Energy values and significant Global Warming Potentials. Since the efficiency of PA-CVD has not yet optimised, the environmental burdens that depend strongly on plant electricity consumption are expected to decrease. Crucial importance assumes the local impacts that are negligible in the case of PA-CVD process but considerable for galvanic treatments due to the emissions of exhaust solutions. However, PA-CVD coatings are very promising for the corrosion protection of metals, as evidenced by the high values of the electrochemical impedance: this justifies the great interest of performing PA-CVD treatments and the up-mentioned crucial role of the functional unit.

Acknowledgement

The authors are grateful for the financial support of the European Commission in the context of MATECO Project 'New coating deposited by PA-CVD for corrosion protection', contract number NMP3-CT-2003-505928.

References

[1] Baldo G.L. (2000) Life Cycle Assessment - Uno strumento di analisi energetica ed ambientale. IPA servizi & ANPA, Italy.

[2] DeBenedetti B., Angelini E., Grassini S., Marino M., Fracassi F., Palumbo F. (2004) Environmental impact and corrosion behaviour assessment of magnesium castings. International Conference on Magnesium, 20-24 September 2004, Beijing, China.

[3] Angelini E., Fracassi F., D'Agostino R., Grassini S., Rosalbino F. (2004) Trends in Electrochemistry and Corrosion at the Beginning of the 21st Century. I. Costa J.M. II. Brillas Enric ed. III. Cabot, Pere-Lluìs ed. IV Collecciò, ISBN: 84-475-2639-9, p.979.

[4] AA.VV. International Journal of Life Cycle Assessment. Ecomed Publishers, Germany, all volumes; http://www.scientificjournals.com.

[5] Angelini E., DeBenedetti B., Grassini S., Maffia L. (2005) Evaluation of environmental impact of protective treatments on automotive magnesium alloys. 2nd International Conference on Heat Treatment and Surface Engineering in Automotive Applications, 20 - 22 June 2005, paper 126, Italy.

[6] Forget L., Delhalle J., Mekhali F. (2001) Investigation of the protective action of chromate coatings on hot-dip galvanized steels. Mater. Corr., 52, 181.

[7] Nazarov A., Thierry D., (1998) Influence of process variables on the corrosion properties of chromate coatings. J. Electrochem. Soc., 145, 39.

[8] Angelini E., d'Agostino R., Di Mundo R., Fracassi F., Grassini S., Laera S., Palumbo F., Rosalbino F. (2005) Tribological and electrochemical characterisation of PA-CVD coatings. 17th International Symposium of Plasma Chemistry, 7-12 August 2005, paper 210.

[9] Fracassi F., D'Agostino R., Palumbo F., Angelini E., Grassini S., Rosalbino F. (2003) Application of Plasma Deposited Organosilicon Thin Films for the Corrosion Protection of Metals. Surf. Coat. Technol., 174-175, 107.