EVALUATION OF THE ENVIRONMENTAL IMPACT OF PROTECTIVE TREATMENTS ON AUTOMOTIVE MAGNESIUM ALLOYS

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ABSTRACT

The Life Cycle Assessment (LCA) approach has been applied to magnesium and magnesium alloys submitted to different protective treatments taking into account also their environmental performances. The study has considered the electrolytic magnesium production starting from Dead Sea carnallite and various coating technologies, as SiO_2-like films deposited by PE-CVD and non-crystalline layers obtained by two different anodising treatments (*reference anodic treatment and k-process patent*).

The LCA preliminary results are very interesting because the Global Warming Potential and the Acidification Potential are 1,5-4 times higher for the anodic coating processes with respect to PE-CVD technology. Moreover, the coating processes have global energetic and environmental loads depending on the shape of magnesium part, which is compared with the impact of the electrolytic magnesium production.

The LCA analysis justifies the great interest of performing PE-CVD treatments on magnesium alloys.

KEYWORDS: LCA, magnesium alloys, PE-CVD, eco-design, corrosion, global warming

INTRODUCTION

The Life Cycle Assessment (LCA) for materials/process/product design is a convenient tool to evaluate different protective treatments of metals and the methodology may be used to supply management strategies with particular attention to the choice between alternative processes.

The life-cycle approach, in this work, has been applied to magnesium and its alloys submitted to different protective treatments. This issue is strategic in the automotive sector where the request of eco-materials is high and the tentative of obtaining a decrease of the environmental impacts both at direct and indirect level is strongly persecuted. Crucial importance assumes the CO_2 reduction target of the European automotive industry imposed by the European Commission (namely the achievement of 140 g of CO_2 per km travelled by 2008 and 120 g of CO_2 per km travelled by 2012)[1] and by other worldwide initiatives that follows the Kyoto Earth Summit and subsequent amendments; all these actions impose a strong reduction of fuel consumption and thus the possibility of improving energy efficiency also by weight reduction.

The EU IPPC Directive (*Integrated Pollution Prevention and Control* – 96/61/CE) is another issue for which the development of best available techniques (BAT) is required as a target of different industrial sectors, including the corrosion protection one.

An extensive employment of magnesium alloys could be a possible solution: Mg is abundant in the earth's crust and its alloys are apt for die-casting and light, but unfortunately, as well-known, prone to corrosion if not submitted to suitable coating processes, possibly clean and environmentally friendly.

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[1] 1997 registered catalytic gasoline fuelled cars (94/12/CE >2.0 l; EURO II) emitted about 400 g/km in urban cycle.

LIFE CYCLE ASSESSMENT TOOL

Life Cycle Assessment is an objective process to evaluate the environmental burdens associated with a process or activity by identifying and quantifying energy and material usage and environmental releases, to assess the impact of those energy and materials uses and releases on the environment and to evaluate and implement opportunities to effect environmental improvements (SETAC, 1991). The framework of this study follows the indications provided by the ISO 14040 series (ISO 14041, ISO 14042, ISO 14043) Standards.

Figure 1 shows a general scheme of the LCA methodology as by ISO 14040: each main phase reported in the figure is here briefly commented.

1. **Goal and scope definition**: it is the preliminary phase in which the aim of the study, the functional unit, the system boundaries, the data categories, the assumptions and the limits are defined.
2. **Life Cycle Inventory**: it is the main section of the work, dedicated to the study of the life cycle of the system product. This phase is mainly concerned with the data collection and calculation procedures and the goal is to provide a detailed description of the raw materials and fuels entering the system (inputs) as well as solid, liquid and gaseous wastes exiting the system (outputs). A software tool is normally used to support the modelling procedures and to provide data base information.
3. **Life Cycle Impact Assessment**: it assists in the understanding of Inventory results, making them more manageable in relation to the natural environment, human health and resources and may identify the relative significance of the Inventory results.
4. **Life Cycle Interpretation**: it is the conclusive phase of a LCA study in which the findings of either the Inventory or the Impact Assessment or both are combined consistent with the defined goal and scope in order to reach conclusions and formulate recommendations. Once the improvements concerning the considered system have been suggested or implemented, the inventory is performed again to see if the expected changes have occurred but also to identify if any unwanted side effects have accidentally been introduced.

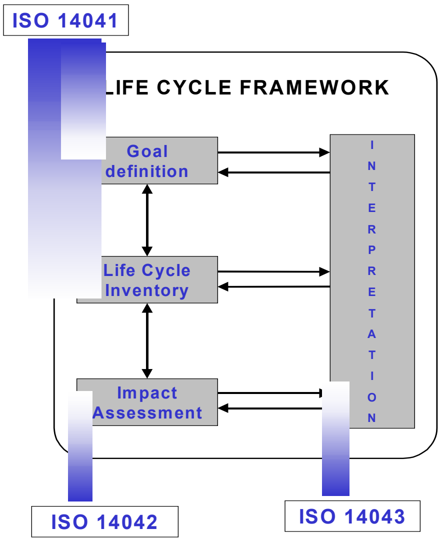


Figure 1 – LCA structure defined by ISO 14040

PROTECTIVE TREATMENTS

Several treatments of magnesium have been developed to improve corrosion resistance, wear resistance and adhesion of paint and adhesive-joining materials. In particular, the objective of this work is to apply the Life Cycle Assessment methodology on the *PE-CVD*, indicated as **P***,* and *K-process*, indicated as **A2**, and to compare them to the reference *anodic process*, indicated as **A1**, since it is the only one used in the Italian automotive industry. Table 1 summarizes the main characteristics of the systems analysed.

A1 *process:* this is an anodising treatment for die-cast and extruded magnesium parts that provides corrosion protection, favourable fatigue properties, good wear properties, very good throwing power down holes. It works also on mixed metal composite (MMC) alloys containing 12% silicon carbide. Adhesion of the coating to the substrate is excellent and the process, easy to operate, does not significantly affect substrate mechanical properties.

The procedure comprises an electrochemical line with associated tanks and power supplies. Products to be coated have to be connected to electrical contacts and immersed into a specific alkaline bath.

A2 *process:* in the technology of this process, a coating is created by a plasma electrolytic oxidation of the substrate. The method is electrolytic: it uses an electrical power supply, in particular a specially modulated AC voltage, and an alkaline bath. The film formed is hard, very adherent, abrasion resistant and has a good corrosion resistance; differently from the usual anodising process it produces harder and thicker layers. Due to the low concentrated alkali electrolyte, which does not contain any toxic elements, the process is environmentally friendly at local level.

P *process:* low-pressure plasma processes, also called cold or not-equilibrium plasmas, are attractive treatment techniques for the surface modification of solid materials. Among these processes, Plasma Enhanced Chemical Vapour Deposition (PE-CVD) of silicon containing organic compounds (i.e. organosilicon) leads to the production of coatings with a wide range of properties by means of a proper selection of the experimental parameters and of the feeding gas composition.

Starting from organosilicon precursors (as hexamethyldisiloxane, hexamethyldisilazane, tetraethoxysilane, etc), it is possible to deposit SiO_2-like thin films (0,01-5 μm) characterized by high chemical and thermal stability and by low gas permeability. Due to the high versatility and the low local environmental impact of PE-CVD this process is particularly promising for the corrosion protection of magnesium alloys. Moreover the plasma approach allows also to carry out substrate pre-treatments just before the deposition process in order to remove surface contamination layers, to perform surface oxidation or reduction as well as to graft on the metallic surface selected chemical species (e.g. fluorine atoms). Pre-treatment are performed in order to obtain a better adhesion to the substrate and to increase the homogeneity degree of the deposited film. It is also possible to deposit multiple and graded layers with chemical composition and properties as a function of the depth.

The deposition process is carried out at room temperature by applying an electromagnetic field in the radio frequency region (13,56 MHz) to a low-pressure ($1 \div 1 \cdot 10^{-3}$ Torr) gas mixture containing the organo-silicon monomer, oxygen and argon.

Electrochemical Impedance measurements performed in aggressive solutions show that, notwithstanding their low thickness, the SiO_2-like films have high protective effectiveness properties against corrosion [1, 2]. An increase of the impedance values, related to an increase in the protective effectiveness, is observed on films obtained at increasing input power and after substrate H_2-plasma pre-treatment.

Table 1 – Main characteristics of coating processes

PROCESS CODE	***A1 process***	***A2 process***	***P process (lab)***
PROCESS TYPE	Non spark	Spark	
COATING RATE (µm /min)	1	2-10	
PROCESS PARAMETER **Electrical Signal** **Current Density (A/dm^2)**	 DC -2	 Pulsed bipolar 2-10	
ELECTROLYTE	High concentration, contains ammonia	Low concentration, alkaline	
TEMPERATURE (°C)	5-20	15-40	
COATING THICKNESS (µm)	5-25	5-50	0,01-5
COATING COMPOSITION	$Mg(OH)_2$ $Mg_3(PO_4)_2$ MgO	$MgAl_2O_4$ MgO	SiO_x-like
SALT SPRAY TEST (not painted samples)	45 h	75 h	25 h
SALT SPRAY TEST (painted samples)	400 h	720 h	350 h

SYSTEM BOUNDARIES AND FUNCTIONAL UNIT

According to ISO 14040, the system boundaries determine which unit processes have been included within the LCA study. Figures 3,4,5 and 6 show the system boundaries of magnesium production, **A1**, **A2** and **P** processes respectively.

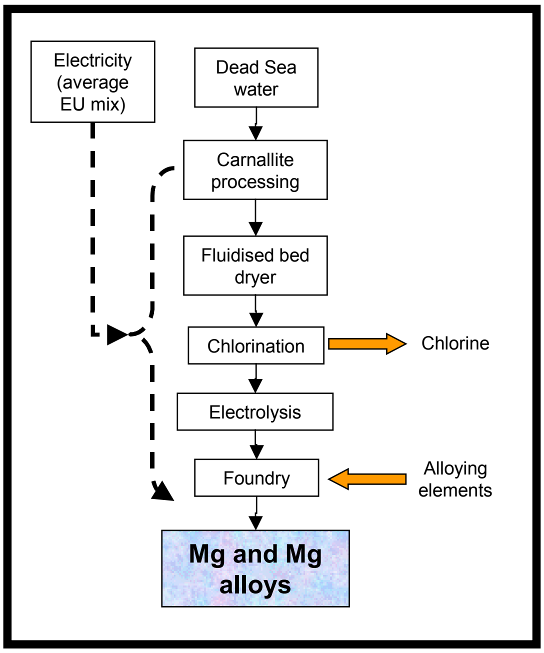


Figure 3 – System boundaries of magnesium production

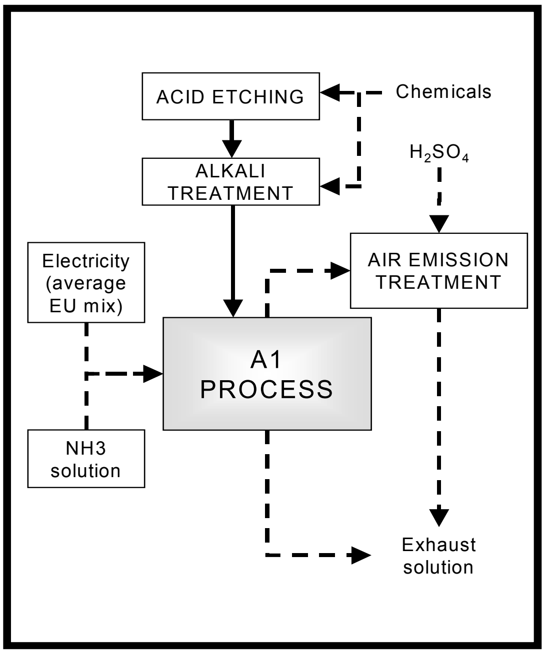


Figure 4 – System boundaries of **A1** process

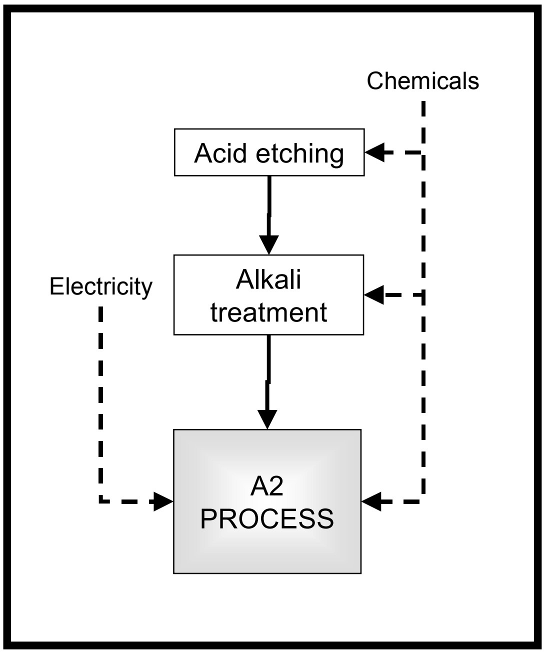


Figure 5 – System boundaries of **A2** process

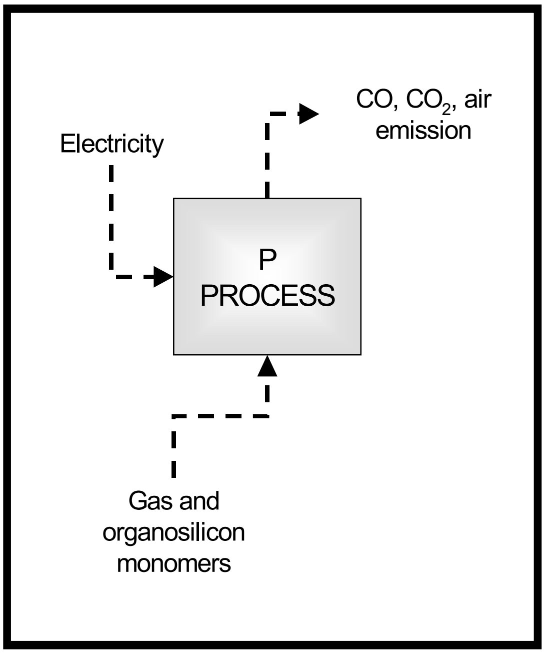


Figure 6 – System boundaries of **P** process

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. Table 2 resumes the functional units associated to the up-mentioned scenarios.

It is particularly important to evidence that in the case of coating technologies, the functional unit should take into account not only geometric characteristics - coated area and thickness - but also layer properties as hardness, wear resistance and, especially, corrosion resistance. Here it is suggested the use of salt spray test as way of comparison for the corrosion resistance of the different coated samples and the consequent transfer to LCA calculations.

The study presents the main results obtained in NANOMAG ("Development of Innovative Nanocomposite Coatings for Magnesium Casting Protection" – Growth Programme n. 40548), a research project sponsored by the European Commission. During project activities, processes have been refined and new data are now available especially as far as coating corrosion resistance properties are concerned.

NANOMAG activities will continue in MATECO project, financed by the European Commission as well. In such context, the follow up of LCA analysis will be carried out using a functional unit in which other properties are taken into account.

Table 2 – Functional units of the analysed processes

PROCESS	***MAGNESIUM***	***A1Process***	***A2Process***	***P Process (lab)***
FUNCTIONAL UNIT	1 kg magnesium ingots	1 m^2 - 20 µm coating surface	1 m^2 - 20 µm coating surface	1 m^2 – 1,5 µm coating surface

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 AND DISCUSSION

The results of the eco-profile analysis are split into the following categories: *energy results*, represented by GER – Gross Energy Requirements, and *environmental results,* using Global Warming Potential (GWP_{100}) and Acidification Potential (AP) impact categories. It is important to remark that the results will be referred to the **A1** process using for each indicator the conventional value (A1 Process = 100).

The LCA analysis clearly shows that GER, Global Warming Potential and Acidification Potential are higher for the anodic coating processes with respect to **P** Process technology. In particular, Table 3 is divided in two parts: geometric results, in which LCA model takes into account only the surface area and the thickness of the coatings, and functional results, in which salt spray tests have been introduced to define a correction factor given by the ratio of the measured corrosion resistance of **A1** Process divided by the corresponding resistance of the examined coating process.

Table 3 – Energetic and environmental burdens (dimensionless parameters, **A1** process=100). The results take into account both geometric and corrosion resistance properties using salt spray tests (not painted samples).

	GER geometric	***GWP_{100} geometric***	***AP geometric***	***R_{corr}***	***Correction factor***	***GER functional***	***GWP_{100} functional***	***AP functional***
A1 Process (1 m^2 – 20 micron)	100	100	100	45 h	45/45 = 1	100	100	100
A2 Process (1 m^2 – 20 micron)	71	62	74	75 h	45/75 = 0,6	42	37	44
P Process (1 m^2 – 1,5 micron)	15	12	16	25 h	45/25 = 1,8	26	22	29

	GER	***GWP_{100}***	***AP***
Mg Production (1 kg)	32	36	40

From the evaluation of the main global environmental impact indicators it can be observed that the **P** process is substantially a clean one, because the main environmental parameters are the electricity consumption and the gas and monomers consumption on the input side, the CO, CO_2, H_2O and air emission on the output side, while in the other processes also high consumption of chemicals as ammonia, sulphuric acid, etc. have to be considered in the input side and emissions of exhaust solutions have to be considered in the output side. Notwithstanding their low thickness, the SiO_2-like films show good protective effectiveness properties against corrosion, which is highly improved by a painting treatment (Figure 7). The samples coated with the **P** process have not requested a previous cataphoresis treatment before painting, which can induce a further improvement of the environmental and economical performances of this process in comparison to the others.

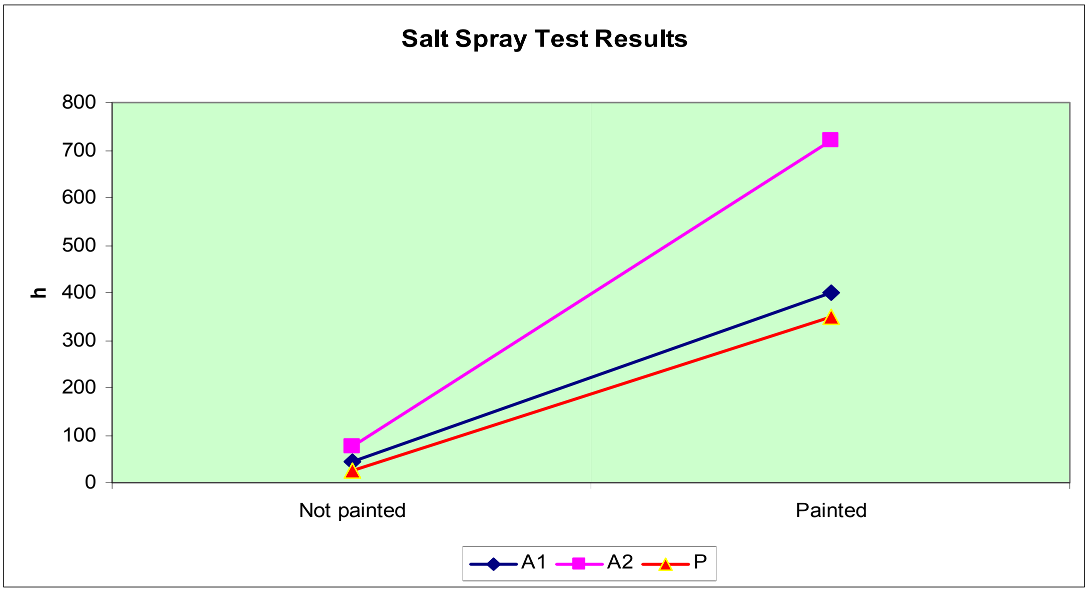
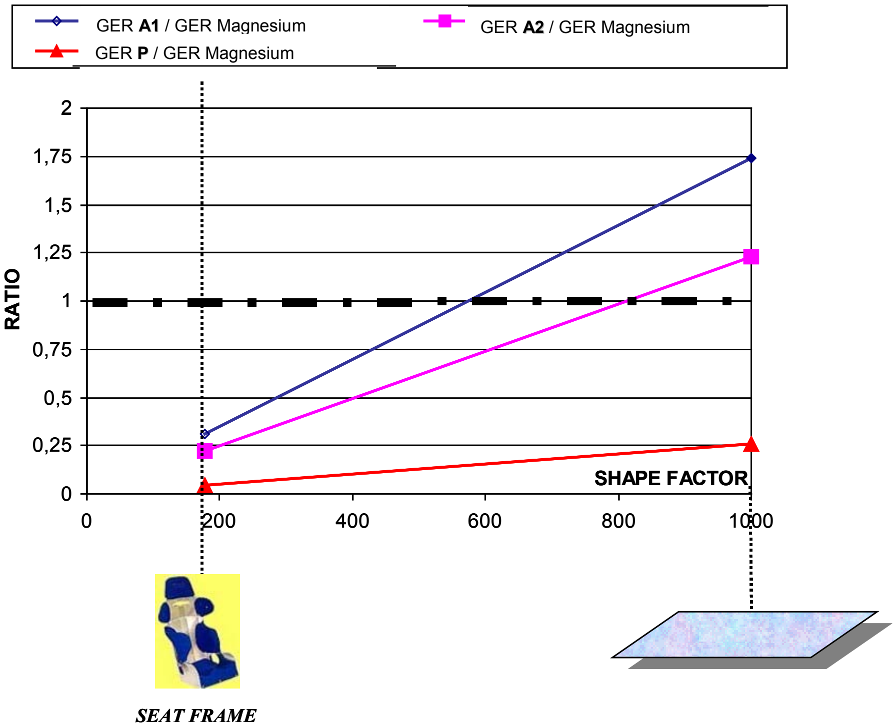


Figure 7 – Corrosion behaviour of samples with and without coating treatment

Furthermore, due to the high-energy consumption of electrolytic magnesium production, the coating processes have relative global energetic and environmental loads depending on the shape of magnesium part. As shown in Figure 8, the influence of coating envi-results has a higher weight when the shape factor increases.



	Seat Frame	*Foil*
Mass (magnesium)	5,4 kg	1,8 kg
Surface (m^2)	0,53	1
Volume (m^3)	0,003	0,001
Shape Factor (m^2/m^3)	177	1000

Figure 8 – Effect of the shape on the envi-results

CONCLUSIONS

Even if the salt spray corrosion resistance is lower for the **P** process coatings with respect to the anodic ones, the LCA analysis shows that the main environmental performances are always better in the case of the plasma treatment, not only if the comparison is made on the basis of the coated surface but also if the salt spray corrosion resistance is considered to define the functional unit.

The global energy requirement is very sensitive to the specific surface area of magnesium parts in the case of the coating technology, because the contribution to GER of the coating has approximately the same weight of the alloy production at shape factor commonly reached in castings. Similar results are obtained considering the other key impact indicators (Global Warming Potential and Acidification Potential). This effect is particularly evident in the case of **A1** and **A2** processes, minor when the **P** process technology is considered.

The SiO_2-like films show good protective properties against corrosion, especially after painting suggesting the need of further evaluation of eco-profiles which take into account this further step.

AKNOWLEDGEMENTS

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