PECVD Coatings for Magnesium Casting Protection

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In this study SiO_2-like *films have been deposited by Plasma Enhanced Chemical Vapour Deposition (PECVD) on Mg alloys employed in the automotive industry in different experimental conditions in order to optimize the protective effectiveness of the deposited layers. The experimental apparatus used was a capacitive coupled (CC) parallel-plate-reactor with an asymmetric electrode configuration, the electromagnetic radiation was applied to a gas mixture containing tetraetoxysilane (TEOS), oxygen and argon in different ratios. The deposition was performed at 100 mTorr of pressure, by varying the input power, on as cast and polished samples submitted to a pre-treatment step in* H_2*-containing plasma. A set of Mg alloy specimens has been treated with a standard anodising process (AP).*

From the overall experimental results, PECVD appears an attractive surface modification technique which allows, through the deposition of SiO_2-like *films, to increase the corrosion resistance of Mg alloys, usually protected with anodising treatment or with chromium-based coatings. The check of the transferability of deposition process to a medium scale range is now running. Magnesium frames representative of real automotive parts coated in a PECVD industrial chamber, assembled and painted are submitted to accelerated corrosion test in order to verify the corrosion resistance of these painted elements manufactured following the production steps of a real component.*

Key words:
Mg alloys, PECVD, SiO2-like films, Corrosion protection, Salt spray test, Electrochemical Impedance Spectroscopy, Automotive industry

INTRODUCTION

The low density of magnesium alloys (1.76-1.84 g.cm^{-3}) makes them especially attractive in order to reach the lowest weight targets, without losing strength, set by the automotive and aeronautical industries.

Almost 90% of magnesium alloys is expected to come in the form of die cast structural components such as instrument panels, seats and steering wheels, etc. where ductility, energy absorption and impact resistance are important in a crash situation.

New casting alloys have been developed with relatively low melting temperatures and good elongation.

These properties speed up the melting and cooling process, increasing the lifetime of expensive dies and making it possible to integrate several components into single large, thin-walled parts.

The rapid flow rates lead to increased productivity at the casting stage and magnesium is known to be very fast, easy and cheap to machine compared with alternative materials. Magnesium alloys have also excellent ductility and therefore can be considered as ideal for impact-resistant safety components and its small draught angle means that high precision castings can often be used straight from the die or with very little machining. The automotive magnesium alloys applications that have received today the greatest worldwide acceptance are steering wheels, instrumental panels, gearbox housings, seats as well as different supports and brackets.

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Unfortunately, magnesium alloys have a strong susceptibility to atmospheric and galvanic corrosion and need to be protected with anticorrosive coatings. Traditionally magnesium and magnesium alloys have been protected with anodising treatments or with chromium-based coatings with the consequent problem of pollution by Cr^{6+} ions. The development of new corrosion resistant coatings for the protection of magnesium parts, by using clean and environmentally friendly processes is very important and strategic for the European industry due to environmental, health and economic considerations: there is a strong need, today, to replace the presently used hazardous coating technologies and to improve the use of light weight materials.

In this context, the thin film technology dealing with non-equilibrium processes for edge surface modifications of materials is gaining increasing popularity, because it allows the modification of the substrate by means of the deposition or modification of thin films in a very versatile way, i.e. by employing low pressure plasmas. The possibility of depositing a wide variety of void-free, well-adherent thin films (100-10.000 angstrom) is one of the most important technological result of the Plasma Enhanced Chemical Vapour Deposition (PECVD) technique.

In this study SiO_2*-like* films have been deposited by PECVD on Mg alloys employed in the automotive industry in different experimental settings in order to find out the best protective conditions.

The transferability of the PECVD deposition process to medium scale range is also evaluated; magnesium alloys frames representative of real automotive parts coated, assembled and painted are submitted to corrosion tests in order to verify the corrosion resistance of painted elements manufactured following every production step of a real component.

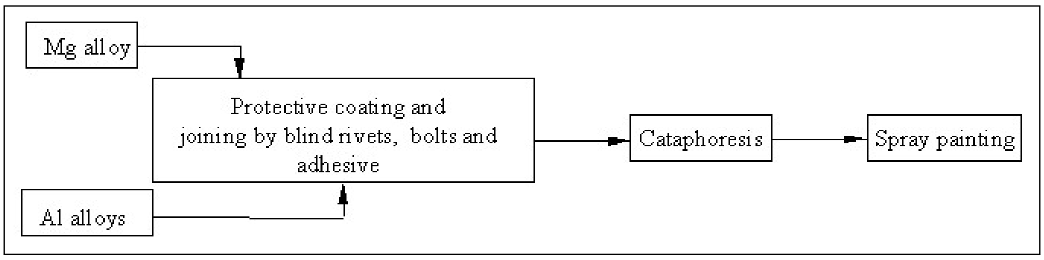

Fig. 1 – Standard automotive assembling and painting cycle.

Fig. 1 – Ciclo di assemblaggio e verniciatura per componenti automobilistici.

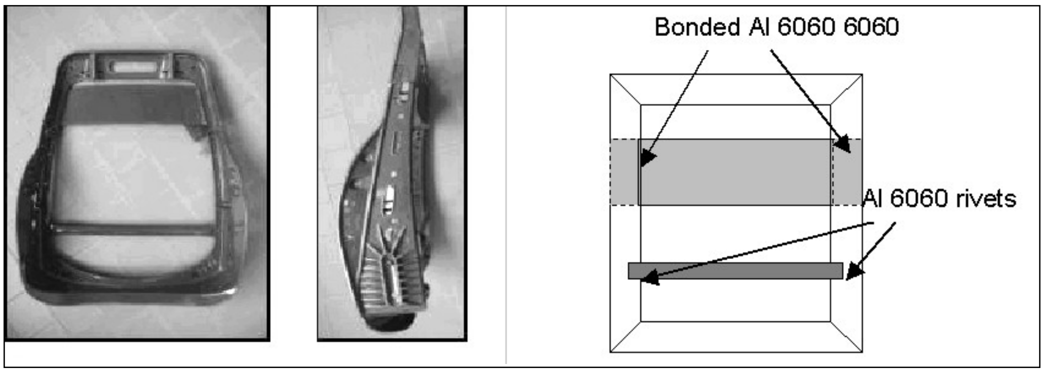

Fig. 2 – Mg seat frame (AM60B) bonded with Al6060 parts, coated by PECVD and painted.

Fig. 2 – Sedile in lega di Mg (AM60B) con parti in Al6060, rivestito mediante PECVD e verniciato.

EXPERIMENTAL

The deposition of SiO_2-*like* films has been carried out on Mg alloy specimens (AM60B) positioned on the grounded electrode of a capacitive coupled parallel-plate-reactor (13,56 MHz), described in details elsewhere [1].

The coatings have been produced at the floating plasma temperature (T<70°C) and 100 mTorr of pressure, by applying the electromagnetic field to a gas mixture containing the organosilicon monomer (tetraetoxysilane - TEOS), oxygen and argon in different ratios (feed composition: TEOS = 2 sccm, O_2 = 0÷45 sccm, Ar = 22÷67 sccm; total flow rate: 69 sccm), in some cases a pre-treatment step has been carried out in H_2-containing plasma (H_2 12 sccm, 50W, 500 mTorr).

The depositions have been performed at 100 mTorr of pressure by varying the input power (50-300W) on as cast and polished samples, cleaned with ethanol in ultrasonic cleaner, in order to remove the high hydrocarbon contamination evidenced by XPS analysis. For comparison purpose, a set of Mg alloy specimens has been treated with a standard anodising process (AP).

The coating/substrate interface has been investigated by X-ray Photoelectron Spectroscopy (XPS). The XPS spectra have been obtained with an ESCA PHI5300 spectrometer by means of non-monochromatic MgKα X-ray source, depth profile mode. The morphological characterization has been performed by optical microscopy (OM) and scanning electron microscopy (SEM). Film thickness has been evaluated by means of a a-step Tencor Profilometer.

The protective effectiveness of AP and PECVD coated samples has been investigated by means of electrochemical techniques, in particular Electrochemical Impedance Spectroscopy (EIS), and salt spray corrosion test (SST), according to ISO 9227 standard method.

The EIS measurements have been carried out in aerated 0.1 M NaCl solution, at room temperature, by using a Frequency Response Analyser EIS300 (Gamry Instruments). Impedance spectra were recorded at the open circuit potential as a function of the exposure time, 1 ≤ t ≤ 200 h, by applying a sinusoidal signal of 10mV amplitude in the frequency range 100 kHz–10 mHz with five points per decade. A three-electrode electrochemical configuration was used with a clamp on electrolyte cell attached by a rubber O-ring. The exposed area of the samples was 12 cm^2. A silver-silver chloride (Ag–AgCl) electrode as reference and a titanium counter electrode were employed. The volume of the test solution inside the cell was 350 cm^2. For comparison purpose the impedance measurements were also performed on bare metal. The experimental data have been analyzed by fitting them to a suitable equivalent circuit model [2-4] in order to obtain the value of the charge transfer resistance, R_{ct}, that can be correlated to the corrosion process occurring at the metal/solution interface and consequently to the deterioration degree of the coating.

AM60B magnesium alloy	**R_{ct} ($\Omega \cdot cm^2$)**
uncoated	60
AP coated	$2.5 \cdot 10^3$
PECVD coated	$1.8 \cdot 10^3$
PECVD coated after H_2 pre-treatment	$7.5 \cdot 10^6$

*Table 1 – Charge transfer resistance, R_{ct}, values recorded on AP and PECVD coated Mg alloys, after 24h of immersion in NaCl 0.1M solution at room temperature. SiO_2-*like *film deposited in the following condition: TEOS = 2 sccm, O_2 = 45 sccm, Ar = 22 sccm, 250W.*

*Tabella 1 – Valori della resistenza al trasferimento di carica, R_{ct}, ottenuti sui campioni di lega di Mg, rivestiti mediante PECVD e trattamento di anodizzazione (AP), dopo 24 ore d'immersione nella soluzione 0,1M di NaCl a temperatura ambiente. Condizioni di deposizione del film SiO_2-*like*: TEOS = 2 sccm, O_2 = 45 sccm, Ar = 22 sccm, 250W.*

In order to assess the compatibility of PECVD films with respect to successive painting cycles, some Mg alloys specimens PECVD coated in the optimized conditions have been submitted to a painting cycle representative of standard automotive assembling and painting procedures shown in Fig.1. A set of Mg alloys samples have been bonded with Al6060 sheets by means of epoxy adhesive or coupled with AlMg5 and stainless steel rivets and bolts. These tests allow also to evaluate the action carried out by the PECVD coatings against galvanic corrosion. As a matter of fact, galvanic coupling effects are particularly detrimental for any industrial component in working conditions.

Furthermore in order to verify the possible scale up of the innovative coating process and in order to investigate the feasibility of the treatment on complex shapes, a series of Mg alloys (AM60B) seat frames, shown in Fig. 2, has been coated by PECVD in an industrial PECVD chamber.

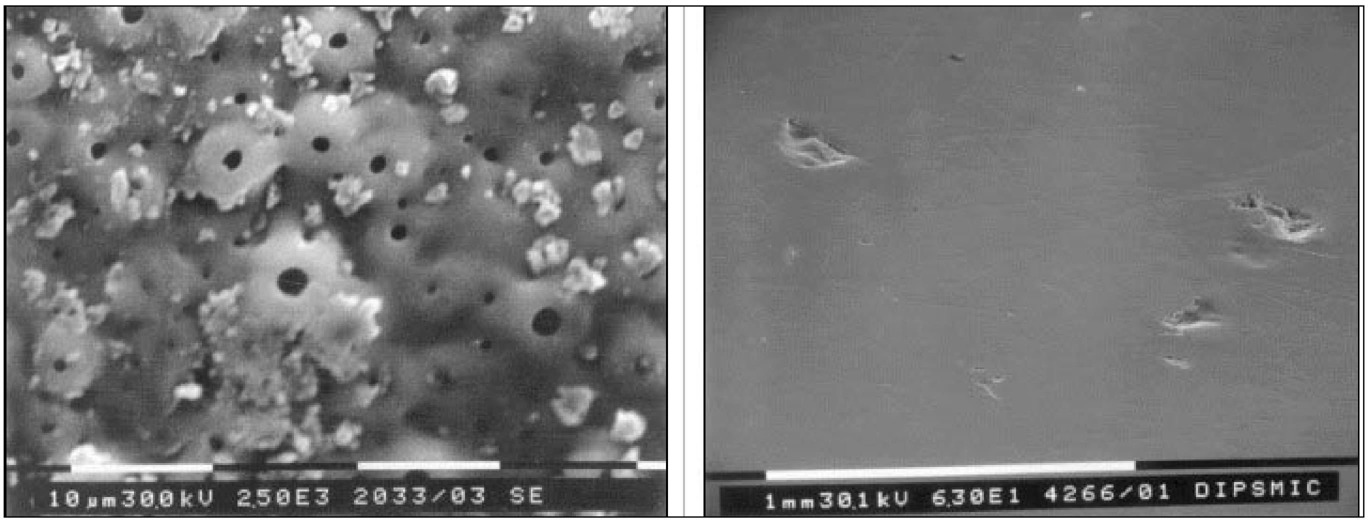

Fig. 3 – SEM micrographs of the surface of AM60B alloy coated with: AP anodising process (left) and PECVD process (right). SiO_2-like *film deposited in the following condition: TEOS = 2 sccm,* O_2 *= 45 sccm, Ar = 22 sccm, 250W, after* H_2*-plasma treatment.*

Fig. 3 – Micrografie SEM della superficie dei campioni di lega AM60B rivestiti mediante trattamento di anodizzazione (sinistra) e PECVD (destra). Condizioni di deposizione del film SiO_2-like*: TEOS = 2 sccm,* O_2 *= 45 sccm, Ar =22 sccm, 250W, dopo trattamento in plasma di* H_2*.*

Successively the AP and PECVD coated seat frames (Fig. 2) have been joined with Al 6060 particulars, painted following the cycle of Fig. 1 and their corrosion resistance has been evaluated by means of the standard salt spray test.

RESULTS AND DISCUSSION

In Table 1 the results of the EIS measurements performed, after 24h of immersion in NaCl 0.1M solution at room temperature, on AM60B specimens submitted to different coating treatments are listed.

The value of R_{ct} determined by fitting the experimental data is 60 Ω·cm^2 for the bare substrate, thus indicating a poor corrosion resistance of the Mg alloy in the aggressive environment considered. A significant increase, two orders of magnitude, of the charge transfer resistance, R_{ct}, is observed for the AP and PECVD coated specimens. By submitting the Mg alloy substrates to a pre-treatment procedure performed in the same experimental setup with H_2 plasma, a further noteworthy increase of the charge transfer resistance is observed.

The R_{ct} values allow to point out the positive role of the H_2 plasma pre-treatment on the protective effectiveness of PECVD thin films, mainly attributed to an improved adhesion on the metal surface.

As pointed out by the XPS analyses in the case of WE43 alloy substrates previously studied [5], the role of pre-treatment in enhancing the PECVD coating performance consists not only in the reduction of organic and hydrocarbon contamination, but also in the reduction of the $Mg(OH)_2$ content, known to be unstable and highly reactive. A slight increase of the R_{ct} value, in comparison to the one of the uncoated alloy, has been observed for AP coated sample (10 µm thick). This poor protection effectiveness can be attributed to the high porosity degree of the coating, as evidenced by the SEM micrograph of Fig.3. Porosities allow the penetration of the electrolyte and favour the beginning of the corrosion process.

On the contrary, notwithstanding the low thickness (1÷2µm), SiO_2-*like* films are very compact, homogeneous and characterised by low defect density (Fig. 3); consequently the PECVD coatings show good barrier effects against the corrosive agents.

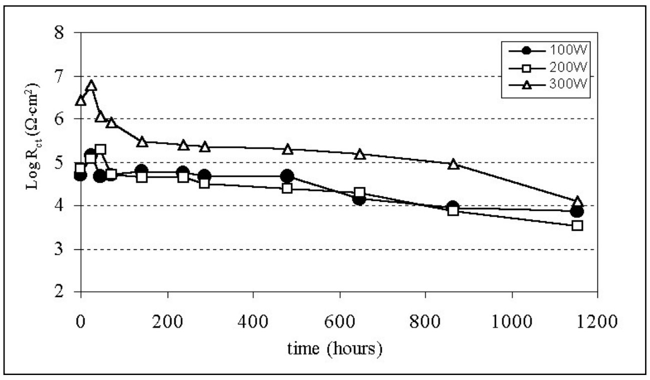

Fig. 4 – Time dependence of R_{ct}*, for AM60B alloy samples coated by PECVD and exposed to 0.1 M NaCl solution.* SiO_2-like *film deposited in the following condition: TEOS = 2 sccm,* O_2 *= 45 sccm, Ar = 22 sccm, 250W, after* H_2 *plasma treatment.*

Fig. 4 – Valori di R_{ct} *in funzione del tempo di immersione nella soluzione 0,1M di NaCl ottenuti sui campioni di lega AM60B rivestiti mediante PECVD. Condizioni di deposizione del film* SiO_2-like*: TEOS = 2 sccm,* O_2 *= 45 sccm, Ar =22 sccm, 250W, dopo trattamento in plasma di* H_2*.*

Best long term corrosion performances have been obtained for polished Mg alloy substrates coated with SiO_2-*like* film deposited in oxygen rich plasma, by increasing the input power, as shown in Fig.4. The value of R_{ct} determined by fitting the experimental data, after 1h of immersion in the NaCl solution, are in the range of 1.2 ·10^4 to 2.8·10^6 Ω·cm^2 for layers deposited from 100W to 300W, respectively. The trend of R_{ct} as a function of the immersion time underlines the good corrosion resistance of the PECVD coated Mg alloys in the aggressive environment considered.

These encouraging results have been confirmed by the salt spray test. As a matter of fact, no evidences of localised corrosion attack have been observed after 48h of exposure to the aggressive environment as shown in the images of Fig. 5.

SiO_2-*like* layers have been deposited in the optimised conditions on Mg as cast sheets, successively submitted to the assembling and painting cycle employed in the automotive industry (Fig. 1).

The impedance measurements carried out on Mg alloy substrate coated by PECVD and painted allow to evidence the good barrier effect of the overall layer, as shown by the high R_{ct} values ranging from 1.0·10^{12} to 1.3·10^9 Ω·cm^2, during 130 days of immersion in the chloride containing environment.

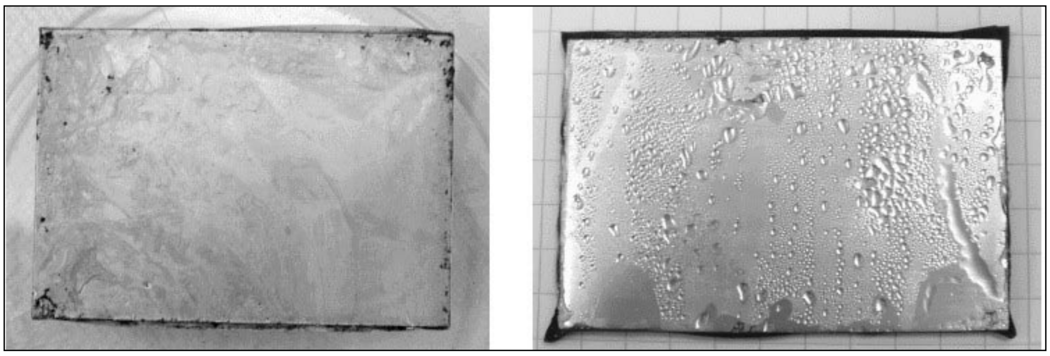

Fig. 5 – AM60B alloy samples after 48h of exposure to SST: as cast (left), PECVD coated in the conditions indicated in Fig 4 (right).

Fig. 5 – Campioni di lega AM60B dopo 48 di esposizione al test in nebbia salina: lega AM60B as cast (sinistra), lega AM60B rivestita mediante PECVD nelle condizioni di Fig. 4.

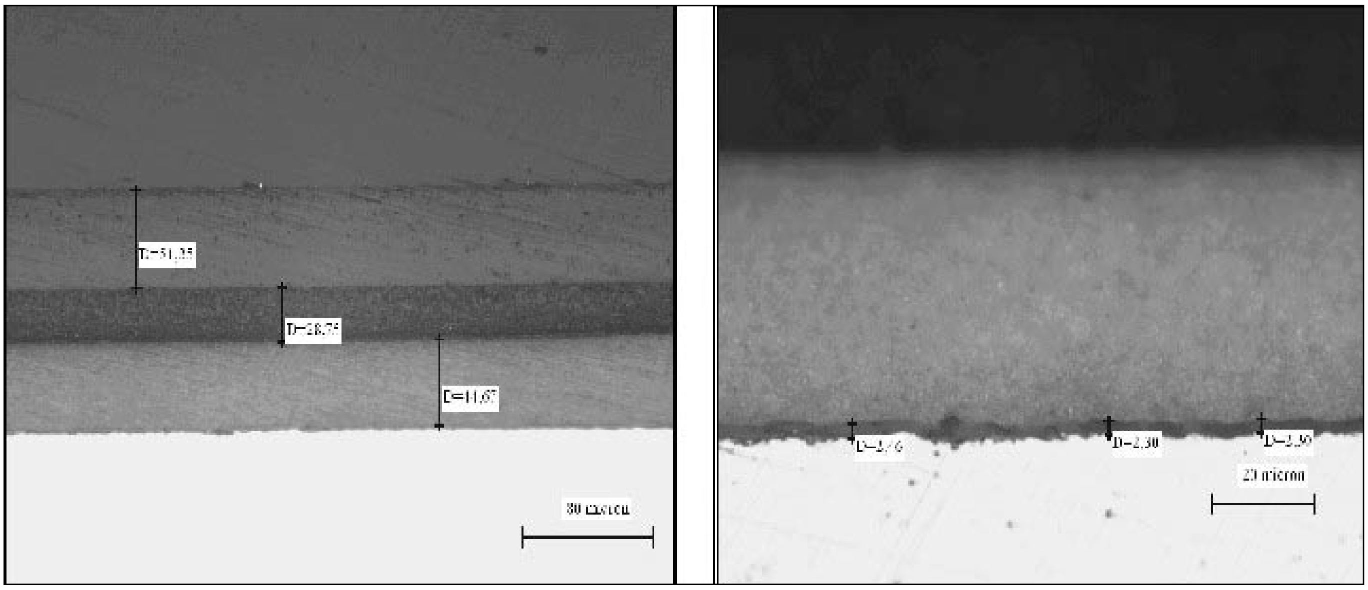

Fig. 6 – OM images of the cross-sections of the AM60B alloy samples: AP coated and painted (left), PECVD coated and painted (right).

Fig. 6 – Micrografie ottiche della sezione di campioni di lega AM60B: campione rivestito mediante processo di anodizzazione e verniciato (sinistra), campione rivestito mediante PECVD e verniciato (destra).

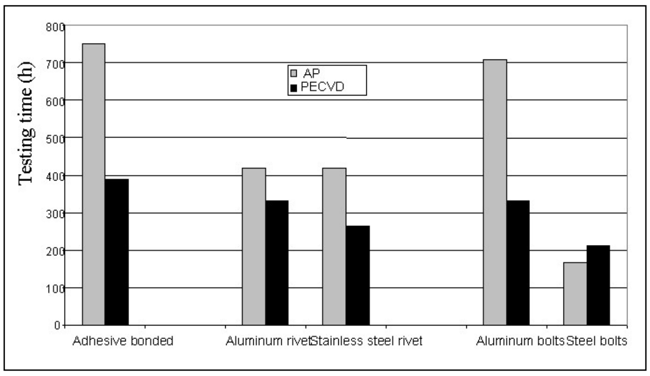

Fig. 7 – Histograms showing the number of hours before corrosion appearance in salt spray test (SST) on Mg alloys specimens, coupled with aluminium and stainless steel rivets and bolts, AP and PECVD coated and painted.

Fig. 7 – Istrogramma relativo al numero di ore in nebbia salina prima della comparsa di segni di corrosione sui campioni di lega di magnesio, con inserti e rivetti in acciaio inossidabile ed alluminio, rivestiti mediante trattamento di anodizzazione e PECVD e verniciati.

The OM images of the cross-sections of PECVD and AP coated and painted AM60B alloy samples are shown in Fig. 6. Both AP and PECVD coatings are well-anchored to the metal surface. No negative effect, such as degassing phenomenon or blowing up on the painting surface, due to the heating during painting cycle may be detected on the layers cross-sections.

The histograms of Fig. 7 summarize the salt spray test results in term of number of hours before corrosion appearance by visual examination of the specimens. Samples joined by mechanical fastening (rivets and bolts) have been coated, subsequently assembled and painted. Samples joined by means of adhesives have been previously bonded, then coated and painted. Due to the insulation of the adhesive layer, the magnesium part of the joining has not been involved in the cataphoresis process as matter of fact PECVD corrosion resistance resulted lower than AP.

Mg alloys samples joined with steel bolts or coupled with Al6060 sheets (steel and AlMg5 rivets) show a noticeable corrosion process after 200h of exposure to the aggressive environment, both if coated with AP and PECVD processes, Fig. 8. Evidences of crevice corrosion have been observed near the jointed areas due to galvanic coupling effects.

AP coated and painted seat frames show good corrosion performances, as a matter of fact only after 478 h of exposure to salt spray test few corrosion signs are detected, as shown in Fig. 9, where also a more extended corrosion attack is observed on a PECVD coated frame. As a matter of fact the protective effectiveness of PECVD coatings on Mg seat frames deposited in the PECVD industrial chamber seems strongly affected by the discharge input power. All coated components show a predominant corrosive attach on the edge of the parts and around the holes. It is predictable that with increasing the input power it will possible to increase the plasma power density and consequently to deposit highly compact and homogeneous layers also on complex shape objects.

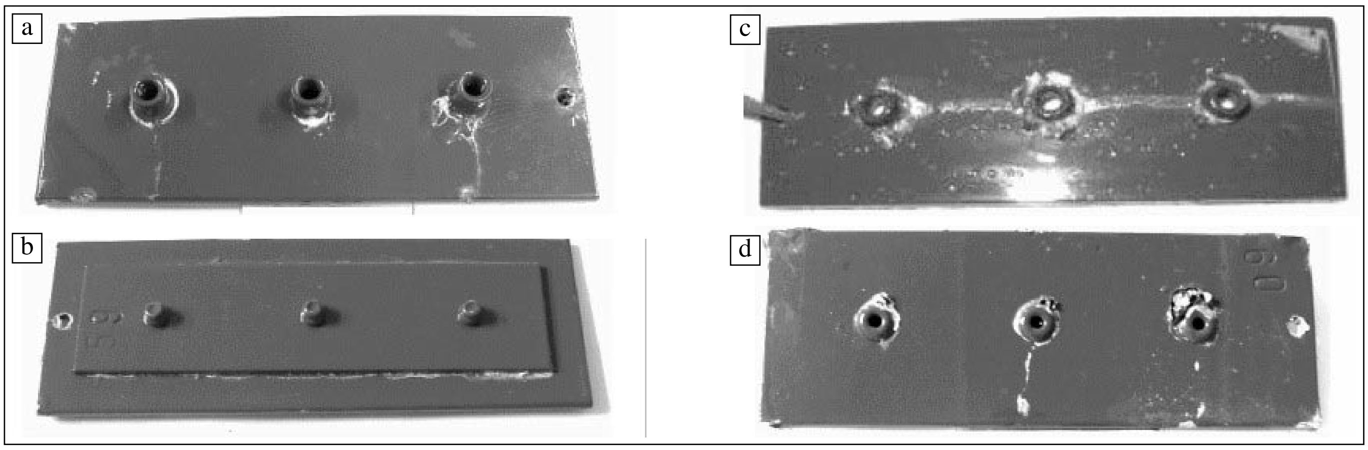

Fig. 8 – Mg alloys samples coupled with steel bolts, Al6060 sheets and AlMg5 rivets: AP coated and painted (left), PECVD coated and painted (right), after 200h of exposure to SST.

Fig. 8 – Campioni di lega di Mg accoppiati con inserti in acciaio, lamine in Al6060 e rivetti in AlMg5: sottoposti ad anodizzazione e verniciati (sinistra), rivestiti mediante PECVD e verniciati (destra), dopo 200 ore di permanenza in nebbia salina.

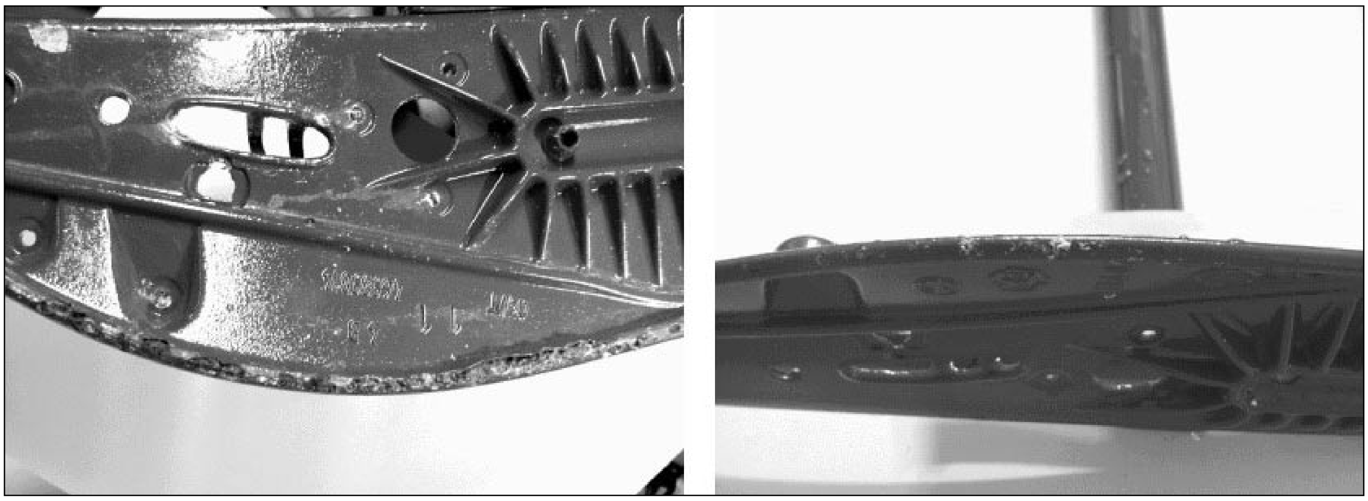

Fig. 9 – Magnesium alloy seat frames after 48h of exposure to SST: PECVD coated and painted (left), AP coated and painted (right).

Fig. 9 – Sedili in lega di magnesio dopo 48 ore di permanenza in nebbia salina: campione rivestito mediante PECVD e verniciato (destra), campione sottoposto ad anodizzazione e verniciato (destra).

A series of experiments is running in order to optimise the PECVD process in the scaled up reactor.

CONCLUSIONS

From the overall experimental results, PECVD appears to be an attractive surface modification technique which allows to increase the corrosion resistance for magnesium alloys, usually protected with anodising treatments or chromium-based coating. Plasma pre-treatment processes have a positive influence on the electrochemical behaviour of deposited film. As a matter of fact, samples submitted to H_2 plasma pre-treatments and coated with SiO_2-*like* film deposited in plasma fed TEOS and O_2, show a significant improvement of the corrosion resistance.

ACKNOWLEDGEMENTS

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ABSTRACT

RIVESTIMENTI PECVD PER LA PROTEZIONE DELLE LEGHE DI MAGNESIO

Parole chiave:
magnesio e leghe,
corrosione, rivestimenti, caratterizzazione materiali,
selezione materiali

Lo sviluppo di nuovi rivestimenti per la protezione delle leghe di magnesio dalla corrosione è un problema economico-ambientale di notevole rilevanza soprattutto in seguito al rinnovato interesse industriale verso l'impiego di tali materiali nel settore aerospaziale ed automobilistico. Le soluzioni attualmente in uso comportano oltre all'incremento dei costi di produzione, un sensibile impatto ambientale, legato in particolare all'inquinamento da ioni Cr6+ conseguente ai trattamenti di cromatazione.
In questo contesto, i processi di modificazione superficiale dei materiali mediante PECVD (Plasma Enhanced Chemical Vapor Deposition) rivestono particolare interesse sia per il basso impatto ambientale, sia per l'elevata versatilità che consente di depositare film sottili SiO_2-like *(100÷10.000 angstrom) le cui proprietà chimico-fisiche, quali inerzia chimica e permeabilità ai gas ed al vapor d'acqua, possono essere modificate variando opportunamente i parametri sperimentali che regolano il processo di deposizione.*
In questo lavoro sono presentati alcuni risultati relativi allo studio del comportamento alla corrosione di substrati in lega di magnesio (AM60B) rivestiti in plasmi a radiofrequenza alimentati con tetraetossisilano (TEOS), ossigeno ed argon.
Il comportamento elettrochimico e la capacità protettiva dei film SiO_2-like *sono stati valutati mediante spettroscopia d'impedenza elettrochimica e prove di corrosione accelerata in nebbia salina in accordo con la normativa ISO9227. I risultati di tali prove sono stati confrontati con quelli ottenuti su alcuni campioni sottoposti ad un classico trattamento di anodizzazione.*
Allo scopo di definire le migliori condizioni operative per il trasferimento del processo PECVD su scala industriale, alcuni provini ed alcuni componenti industriali rivestiti con il film SiO_2-like *sono stati sottoposti ad un ciclo di assemblaggio e verniciatura impiegato nell'industria automobilistica (Fig. 1, 2). L'accoppiamento dei substrati di lega AM60B con particolari di acciaio inossidabile e/o di lega di Al (Al6060, AlMg5) ha, inoltre, permesso di valutare il comportamento dei rivestimenti PECVD nei confronti dei fenomeni di accoppiamento galvanico, particolarmente critici per i componenti industriali in condizioni di esercizio.*
Le misure d'impedenza elettrochimica (Tab. 1) e le analisi dell'interfaccia film/substrato condotte mediante spettroscopia XPS hanno evidenziato come la messa a punto di un pre-trattamento della superficie in plasma d'idrogeno, sia fondamentale al fine di incrementare l'adesione del rivestimento al substrato. Infatti il pre-trattamento consente di eliminare i contaminati organici presenti sulla superficie metallica e di ridurre il tenore di $Mg(OH)_2$ *particolarmente reattivo nei confronti di eventuali agenti aggressivi. Il significativo incremento della resistenza al trasferimanto di carica,* R_{ct}, *registrato per i campioni rivestiti mediante PECVD è da correlarsi all'omogeneità ed al basso grado di difettosità dei film* SiO_2-like *come confermato dalle osservazioni condotte al microscopio elettronico a scansione (Fig. 3). Al contrario, il rivestimento ottenuto mediante trattamento di anodizzazione mostra un alto grado di porosità e conseguentemente una minore capacità protettiva.*
Lo studio condotto ha evidenziato come le proprietà barriera dei film SiO_2-like *dipendano, in particolare, dalla potenza di scarica e dalla composizione della miscela di alimentazione. Buone proprietà protettive sono state evidenziate per i film depositati ad alta potenza in plasmi ricchi di ossigeno (Fig. 4, 5).*
Infine, il processo PECVD ha evidenziato una buona compatibilità con il ciclo di verniciatura industriale. Infatti, non sono stati evidenziati segni di alterazione del film SiO_2-like *durante le fasi di riscaldamento previste dal ciclo stesso; il film consente inoltre di ottenere una buona adesione della vernice al substrato metallico (Fig. 6, 7). Fenomeni di corrosione interstiziale sono stati evidenziati sui provini in corrispondenza delle zone di contatto con le parti in acciaio inossidabile e in lega di Al dopo 200 ore di esposizione alla nebbia salina.*
Risultati incoraggianti sono stati ottenuti anche nelle prove di corrosione accelerata effettuate sui componenti reali. Tuttavia, lo scale-up del processo richiede un'ulteriore fase di messa a punto al fine di poter depositare rivestimenti con elevata capacità protettiva anche su oggetti di forma complessa (Fig. 9).