Evaluation of corrosion resistance of biocompatible coatings on magnesium

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The work deals with the study of innovative biocompatible coatings for magnesium resorbable osteosynthesis devices. Conversion layers based on magnesium fluoride and "diamond like carbon" coatings (DLC) obtained by chemical vapor deposition were considered in order to reduce the corrosion rate of magnesium to levels compatible with the time needed for fracture healing. DLC coating was applied on both pure magnesium and on magnesium after conversion treatment in hydrofluoric acid. Weight loss tests and potentiodynamic polarization tests in aerated Hank's solution at room temperature were performed. The corrosion rate was about 100 mg/cm^{2}day for the commercially pure magnesium (99.9 %) in the first 24 hours of exposure. Both the coatings reduced the short-term corrosion rate but the protective layers did not grant long-term stability and corrosion rate rapidly increases approaching the values of uncoated magnesium.

Keywords: Corrosion - Magnesium - Biocompatible coating - DLC coatings - Resorbable osteosynthesis devices

INTRODUCTION

Annually, several million people suffer bone fractures caused by accidents or diseases. Many of those fractures are too complex for an external medical treatment but have to be surgically stabilized by osteosynthesis devices (intramedullary nails, plates, screws, pins etc.). Traditional methods of osteosynthesis or osteotomy use permanent metal implant devices. However, they have several significant drawbacks. First, after the fracture healing, a successive operation is often necessary to remove the implants – especially in pediatric patients - with several risks such as infection, removal problems of jammed implants, implants migration, and related extra health care costs. Secondly, metal devices cause magnetic resonance imaging artifacts producing visualization difficulties for tissue regeneration monitoring. Finally, the high modulus of elasticity of metals compared to bone results in the implant retaining a large fraction of the mechanical load. This is known as "stress shielding" effect, which leads to bone reabsorption, implant loosening, and, consequently, the need of further surgical intervention.

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The use of resorbable osteosynthesis devices could be extremely beneficial in orthopedic surgery because it avoids the removal of fixation implants. A biodegradable bone fixation implant should provide stability for the period corresponding to the time needed for fracture healing, with a service-life longer than 3-4 months, which is the time for new bone formation and restoration. Afterwards, it can dissolve or be absorbed in the body. Several materials have been proposed as bioresorbable osteosynthesis devices; particular attention has been paid since the early twentieth century to magnesium, which has a suitable specific modulus and sufficient tensile strength. Furthermore, ions released due to magnesium corrosion are not dangerous in human body because they take part in many metabolic reactions and biological systems, including the formation of biological apatite crystals, which is important for metallic bone implants consolidation [1]. It is also a cofactor for many enzymes and stabilizes the structures of DNA and RNA [2]. It has been shown that magnesium apatite precipitates on magnesium surface [3-4] and osteoblast responds to the degrading magnesium alloys in femur of guinea pig [5]. Unfortunately, magnesium rapidly dissolves in human body fluids giving an early decay in terms of mechanical integrity before bone healing [6].

The literature data on corrosion rate of magnesium are generally conflicting due to experimental difficulties and electrochemical behavior of magnesium [7]. Song et al. [8] founded dissolution rate of pure magnesium in the range of 19-44 mg/cm^2 day in solution simulating body fluids. Brar et al. [9] reported that the corrosion rate decreased

from 2.64 mg/cm^2 day just after immersion to about 0.48 mg/cm^2 day after 24 hours exposure. Kirkland et al [10] obtained values ranging from less than 1 to 2 mg/cm^2 day for the high-purity magnesium (99.99%) as a function of exposure time. The same authors emphasize corrosion rates of commercially pure magnesium with title of 99.9% one order of magnitude higher than high-purity magnesium [9-12]. Such rates can produce large amount of hydrogen that could be detrimental for the patient.

The dissolution rate could be controlled by means of protective coatings. The industrial methods for protection of magnesium through coatings usually consist on chromates conversion layers as base for subsequent painting cycles. This approach is not suitable in the human body. In order to reduce corrosion rate and stimulate bone restoration, some authors [13-15] proposed protective coatings based on calcium hydroxyapatite, calcium phosphate and calcium fluoridate hydroxyapatite for this application. Such techniques are surely very promising but further studies are still needed [16]. Chiu et al reports corrosion rate reduction of about 40 times of magnesium after conversion treatment by immersion in 48% hydrofluoric acid for 24 hours [17].

"Diamond Like Carbon" coatings (DLC) have high hardness, low friction coefficient, chemical inertness, high electrical resistivity, high transparency and water resistance. Such properties make them ideal for biomedical implants coating. Preliminary tests in vitro and in vivo demonstrated DLC adhesion on a wide range of biomaterials without toxic or inflammatory effects on the surrounding cells [18]. DLC coatings on magnesium have been obtained with different techniques by Sella et al, Matsufumi and Walter et al. [19-21].

The aim of this work is the preliminary study on the effects of conversion coatings in hydrofluoric acid and DLC on the corrosion rate of magnesium. The results of weight loss and potentiodynamic tests in Hank's simulating body fluid solution are presented.

EXPERIMENTAL

The tests were carried out on pure magnesium disks (99.9%, maximum presence of 280 ppm of Fe, 170 ppm of Mn, 70 ppm of Al, 50 ppm of Si, 20 ppm of Zn and 10 ppm of Ni) with a diameter of 15 mm and a thickness of 1.5 mm. The specimens were polished with emery papers up to 4000 grit and then passivated in air for 48 hours before testing or the application of the DLC coatings. The conversion treatment was performed immediately after the sample polishing. Fluoride coatings were obtained by chemical conversion in 50%, hydrofluoric acid for 24 h at room temperature according to the method suggested by Chiu et al. [17]. The specimens were then washed with distilled water, degreased in ultrasonic bath with acetone for 10 minutes, and finally air-dried. The conversion treatment produces an adherent dark layer on the specimen surface.

Si-DLC/DLC coating was deposited by RF-PECVD (Radio Frequency Plasma-Enhanced Chemical Vapor Deposition) using a mixture of argon (Ar 99.999% pure), methane (CH$_4$ 99.999% pure) and Hexamethyldisiloxane vapors (HMDSO grade >99.5%). Deposition was performed at 50°C in a capacitive coupled parallel plates reactor having grounded sample holder, and gas shower connected the RF generator which ignited plasma at mid-low frequency (50 kHz). Before the deposition, samples underwent a soft plasma etching process in argon for 15 minutes. An intermediate Si-DLC layer have been obtained by adding an HMDSO vapor pressure to the gas mixture for 180 minutes; the final pure DLC layer has been obtained in Ar/CH$_4$ plasma for 30 minutes. All the depositions were carried out at 16.56 MHz frequency. DLC coating was deposited on both metallic surface and after chemical conversion treatment in hydrofluoric acid.

Standard aerated Hank's solution was considered to simulate human body fluids [22]. The pH of the solution is in the range 6.6-6.85 before testing. All the tests were carried out at room temperature.

Electrochemical tests were carried out in ASTM G5-82 standard cell on specimens with an exposed surface area equal to 0.785 cm^2. Potentiodynamic tests were performed after 120 s of stabilisation at open circuit potential (OCP). The scan rate was 1 mV/s from -10 mV vs OCP to 0.5 V vs SCE. During the stabilization period, the open circuit potential was monitored.

Weight loss tests were performed at different exposure times. The specimens extracted from the testing solution have been rinsed in distilled water and ultrasonic-cleaned in acetone for about 3 minutes, then air-dried and weighed. The corrosion rate (V_{cor}) was derived by normalizing weight loss (M) to the exposed surface area (S) and testing time (t)

$$V_{cor} = \frac{M}{S \cdot t} \qquad (1)$$

RESULTS

Morphology of coating

The morphology of coating was analyzed through scanning electron microscope and EDS to evaluate homogeneity and defects. The conversion layers do not show homogeneous appearance and it is characterized by uniform wide zones covered by compact magnesium fluoride alternated by magnesium oxide areas distributed along the grain boundary of substrate (figure 1).

The DLC coating deposited directly on the surface of magnesium is uniform, compact and tight, with a thickness of about 2-2.5 μm (figure 2a). On the specimens previously covered by magnesium fluoride conversion layer (MgF$_2$/DLC), the DLC coating has thickness of approximately 1.2-1.6 μm and defects at the interface were noticed due to the presence of magnesium oxide at the grain boundary (figure 2b).

Weight loss tests

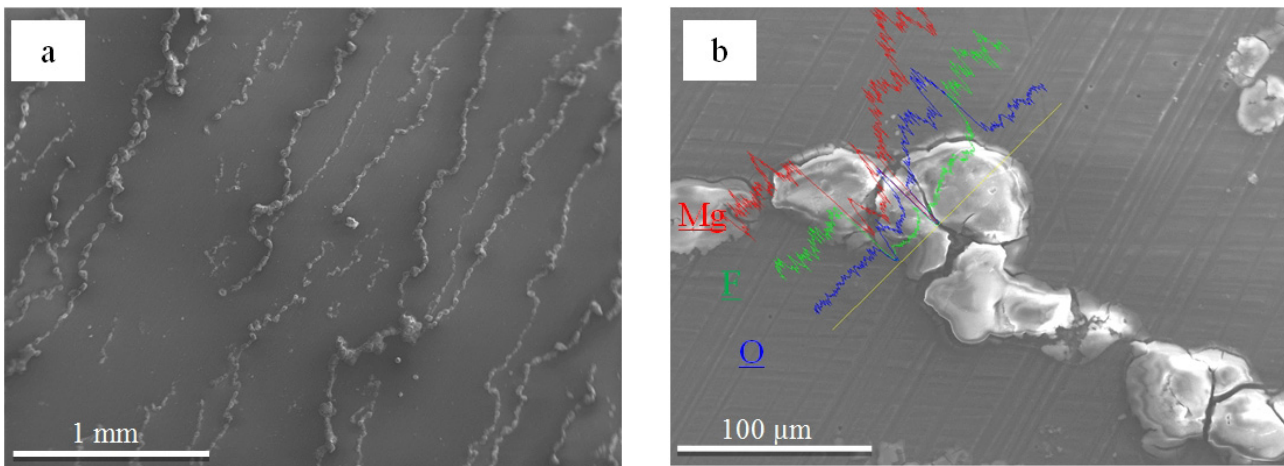The residual weight of specimens after immersion in the

Fig. 1 - SEM morphology of the fluoride conversion coating (a) and EDS magnesium, fluorine and oxygen profiles on film defect at the grain boundaries (b)

Fig. 1 - Osservazione al SEM della morfologia dello strato di conversione a base di floruro (a) e profilo EDS del magnesio, fluoro e ossigeno in corrispondenza dei difetti a bordo grano (b)
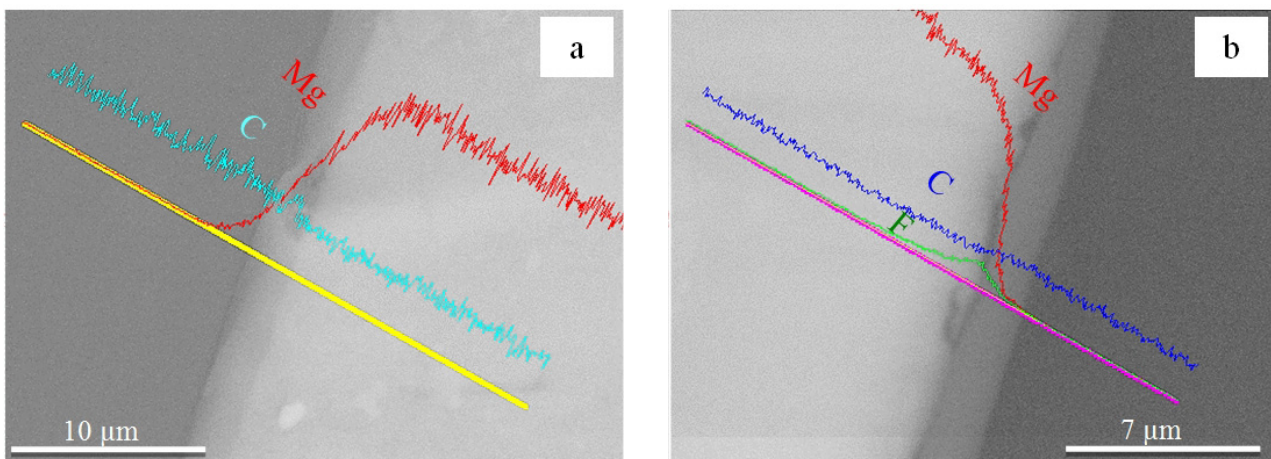

Fig. 2 - EDS line profile of DLC coating on bare magnesium (a) and magnesium with fluoride conversion layer (b)

Fig. 2 - Profili EDS di composizione del rivestimento DLC su magnesio (a) e su magnesio con uno strato di conversione di floruro (b)

Hank's solution was normalized to the initial value. Figure 3 shows the normalized weight as a function of the exposure time. In the first minutes, the uncoated specimens show a slight increase in weight due to the formation of a thick layer of corrosion products. The weight decreases very quickly for exposure longer than three hours and the specimens completely dissolved after 24 hours. The average corrosion rate in the first 19-24 hours is about 100 mg/cm^2 day (Figure 4), considerably higher than reported by Song et al. [8].

Similar values were obtained by other authors in chloride-containing solutions [22].

The weight loss decreases on specimens covered by conversion treatment in hydrofluoric acid: after 19 hours of exposure, the weight loss is less than 4% and less than 14% after 24 hours, corresponding to 5 and 14.5 mg/cm^2 day corrosion rate, respectively (Figure 3 and 4). Despite the reduction of corrosion rate, the coated specimens completely dissolved after just 48 hours. On DLC coating, the weight loss was only estimated on a single specimen, at the end of the free corrosion potential monitoring - which was continued for 21.5 hours - until perforation occurred. Corrosion rate about 35 mg/cm^2 day was estimated which is intermediate between uncoated magnesium and magnesium coated by conversion layer.

Electrochemical tests

Figure 5 shows the potentiodynamic anodic curves in Hank's solution. The corrosion potential reaches much more negative values on uncoated magnesium, which rapidly stabilizes in the range 1.7-1.8 V vs SCE. Localized attacks at the end of the test were noticed. The corrosion potential of the specimens treated in hydrofluoric acid stabilizes quickly at more noble values than uncoated

specimens, between -1.55 and -1.51 V vs. SCE. Corrosion attack initiates in correspondence of the discontinuities of the film and then propagates on the whole surface.

DLC coated samples showed different behavior mainly depending on the coating defectiveness. The specimens with uniform coating showed very noble free corrosion potential values - close to 0 mV vs SCE – just after immersion. The potential quickly drops below -0.5 V vs. SCE which is approximately 1 V above the values of the uncoated specimens and specimens with the fluoride conversion treatment. Preferential corrosion attacks initiate in correspondence with coating defects, influencing the reproducibility of experimental results. In such zones, the substrate rapidly dissolve producing a severe localized attack, which can be clearly evidenced at the end of the test. The unattacked surface of the specimen is still completely covered by the coating (Figure 5).

Due to the intrinsic defectiveness of coating, MgF_2/DLC specimens showed free corrosion potential values close to that measured on uncoated magnesium.

The polarization resistance (Rp) was calculated from potentiodynamic curves as the slope at the free corrosion potential in order to estimate corrosion rate after few minutes of exposure. Corrosion current density (icor) was calculated by the Stern and Geary relationship:

$$i_{cor} = \frac{k}{R_p} \qquad (2)$$

The value of the constant k was assumed equal to 39 mV according to literature data [23]. Corrosion current densities are in the range 0.13-0.33 A/m^2 (corresponding to 0.14 to 0.36 mg/cm^2day) for uncoated magnesium, 0.018 A/m^2 for the magnesium with the fluoride coating (corresponding to 0.02 mg/cm^2day) and 0.14 A/m^2 for the DLC coated magnesium (corresponding to 0.15 mg/cm^2 day). Good correlation with the corrosion rates estimated by weight loss tests just after immersion can be observed. After a few hours of immersion, the corrosion rate calculated by weight loss is two orders of magnitude higher than the value calculated by polarization resistance.

DISCUSSION

The high dissolution rates - reaching 100 mg/cm^2 day - measured on magnesium after 24 hours of exposure reflects the highly reactive nature of this metal. At the very negative corrosion potentials of the magnesium, the cathodic process of hydrogen evolution supports the attack with very fast kinetic on cathodic areas that in the commercially pure magnesium are mainly represented by the impurities. Magnesium is a metal with high hydrogen overvoltage and its corrosion rate principally depends on the presence of more noble elements with low hydrogen overvoltage, such as iron and manganese, even if in small quantities. Thus, the results confirm on commercially pure magnesium in simulate human body solution corrosion rates higher than values reported in the literature on high-
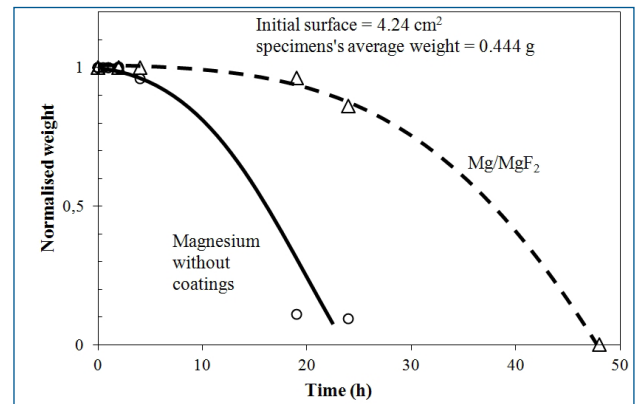

Fig. 3 - *Weight loss normalized to the initial weight of specimen as a function of exposure time*

Fig. 3 - Variazione di peso dei provini normalizzata al peso iniziale in funzione del tempo di esposizione.
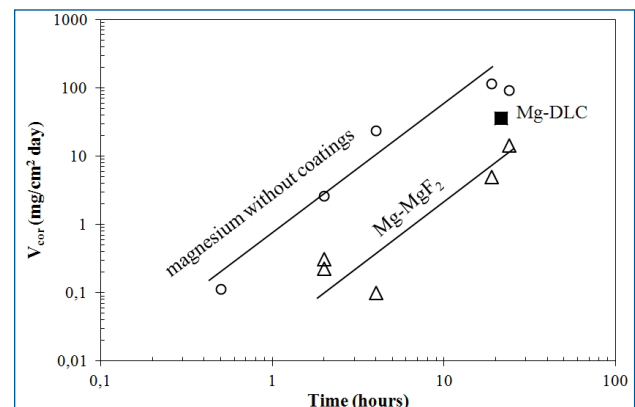

Fig. 4 -*Average corrosion rate as a function of exposure time*

Fig. 4 - Velocità di corrosione media nel periodo di esposizione in funzione della durata di questa

purity magnesium [8].

During early exposure - immediately after immersion in the solution - the dissolution rate of magnesium increases due to the reactivation of the originally passive surface. Actually, magnesium hydroxide film spontaneously formed in air protects the metallic surface. Thus, the corrosion resistance of magnesium is related to the stability of this film. The $Mg(OH)_2$ layer is stable in alkaline solutions [23] but it spontaneously dissolves in solution with pH below the neutrality. The high reactivity of commercially pure magnesium in Hank's solution is mainly caused by the presence of chloride ions, since they form a very soluble chloride salt, which makes unstable the hydroxide film according to the reaction [10, 12]:

$$Mg(OH)_2 + 2Cl^- \longrightarrow MgCl_2 + 2OH^- \qquad (3)$$
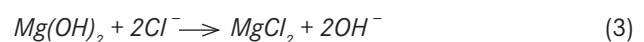
Magnesium begins to dissolve with relevant hydrogen evolution and formation of soluble chloride salt and alkalinity

according to reaction (4)

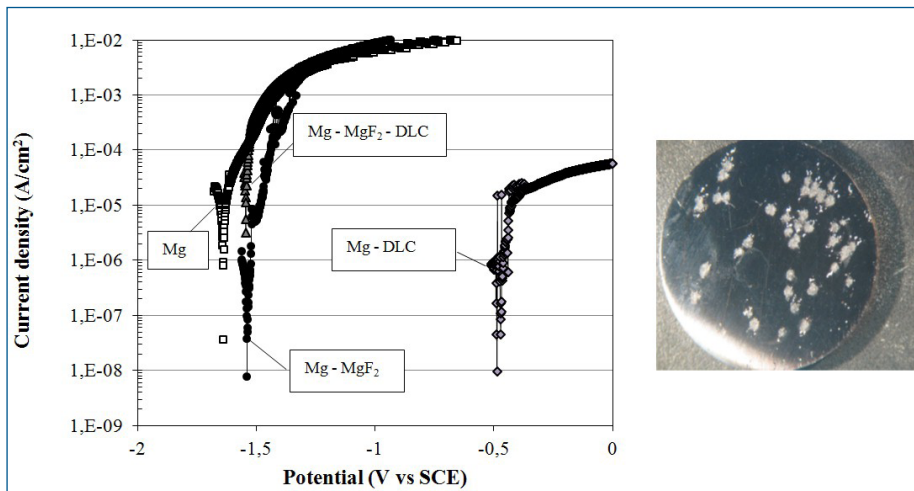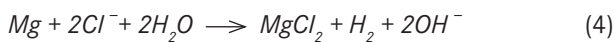$$Mg + 2Cl^- + 2H_2O \longrightarrow MgCl_2 + H_2 + 2OH^- \qquad (4)$$

The intense bubbling stirs the diffusion layer at the metal/solution interface preventing the strong alkalization produced by magnesium corrosion and any restoration of magnesium hydroxide film. Consequently, very rapid dissolution occurs.

The protection offered by conversion layers obtained by immersion in hydrofluoric acid is due to the precipitation on the surface of not soluble magnesium fluoride (MgF_2). This salt has low solubility product, equal to $5.2 \cdot 10^{-11}$. The film is not electrically conductive and behaves as passivation film more stable than magnesium hydroxide film so that the dissolution in the Hank solution takes place over a double time with respect to uncoated magnesium. However, the fast formation of $MgCl_2$ initiates from the defects along the grain boundary of substrate, where magnesium oxide grows through the fluoride layer (figure 1), and then extends to the entire surface.

The DLC coatings behave in a different way compared to the conversion layers of magnesium fluoride. Just after immersion, the specimens with continuous DLC coating showed OPC potentials close to the redox potential of oxygen. Thus, in the early period the coating surface seems to act as very noble electrode, demonstrating some electrical conductivity in the layer. Unfortunately, we could not perform direct measurements of the electrical properties. Nevertheless, it is plausible to assume a certain conductivity. The electrical properties of diamond-like carbon films can vary from that of a semimetal to that of an insulator, depending on the deposition conditions and incorporation of metals or nitrogen in the film [24]. Therefore, the film has a more noble behavior than magnesium and acts as a cathode in the film to substrate coupling.

However, after the early period, the potential rapidly decreases. In correspondence of the discontinuities of the film, activation of corrosion on metallic surface produces very deep penetrating attack due to unfavorable ratio between small anodic areas and large external cathodic surface. The overall dissolution rate of magnesium is li-

mited by the confinement of the DLC coating, leading to an intermediate behavior between the uncoated magnesium and specimens with fluoride conversion coating. The hydrogen bubbles evolution caused by the corrosion process increases and coating is detached in correspondence with the interface. General corrosion then occurs for longer exposure.

CONCLUSIONS

Corrosion tests were carried out on bare and coated pure magnesium in simulating body fluids solution to evaluate the use for bioresorbable osteosynthesis devices. The results confirm high dissolution rates on commercially pure magnesium, reaching 100 mg/cm^2 day in Hank's solution. They highlighted the possibility to reduce the corrosion rate of commercially pure magnesium by the deposition of magnesium fluoride-based conversion layers and with diamond like carbon coatings (DLC). The experimental observations emphasize the role of the coating defects - which were detected by the morphology analysis - in the dissolution dynamic of coated specimens.

Different behavior was noticed between the two different coatings with galvanic coupling between DLC layer and substrate.

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Valutazione della resistenza alla corrosione di rivestimenti biocompatibili su magnesio

Parole chiave: Magnesio e leghe - Corrosione - Caratterizz. Materiali

Lo scopo di questo lavoro è lo studio di rivestimenti biocompatibili in grado di rallentare la velocità di corrosione del magnesio per produrre mezzi di osteosintesi riassorbibili biocompatibili. Sono stati considerati strati di conversione a base di MgF_2, ottenuto per trattamento in acido fluoridrico, e rivestimenti "Diamond Like Carbon" (DLC), quest'ultimi applicati sia sul magnesio puro sia su magnesio dopo un primo trattamento di conversione. Lo strato di conversione si presenta con ampie zone ricoperte in modo uniforme da MgF_2 e isole di $Mg(OH)_2$ affioranti al bordo di grano del substrato (figura 1). Il rivestimento DLC applicato su magnesio appare uniforme, con spessore di circa 2-2.5 μm, mentre quello sui provini dopo trattamento di conversione (MgF_2/DLC) è discontinuo e di spessore inferiore (circa 1.2-1.6 μm) (figura 2). La dissoluzione del magnesio nella soluzione di Hank è dapprima relativamente contenuta; dopo tre ore i provini perdono rapidamente peso e si sciolgono completamente prima di 24 ore. La velocità di corrosione media nelle prime 19-24 ore è di circa 100 mg/cm^2 giorno. La perdita di peso diminuisce nei provini sottoposti al trattamento di conversione in HF, tuttavia, anche in questo caso, i provini sono disciolti completamente dopo 48 ore (figura 3). Per i provini con il rivestimento DLC la velocità di corrosione è pari a circa 35 mg/cm^2 giorno, intermedia rispetto al magnesio non rivestito e al magnesio con lo strato di conversione (Figura 4). La figura 5 riporta le curve potenziodinamiche per i provini nelle diverse condizioni. La velocità di corrosione calcolata mediante la resistenza di polarizzazione sui provini dopo breve immersione sono in linea con quelle dalle perdite di peso a tempi brevi. Il rivestimento DLC è molto più nobile rispetto al substrato e causa la corrosione per effetto galvanico nei punti di discontinuità (figura 4b). La riduzione dell'area totale esposta riesce, tuttavia, a ridurre la velocità di corrosione complessiva del magnesio nei primi istanti di immersione, quando il rivestimento è ancora presente. Il rivestimento di MgF_2 non ha un comportamento catodico nei confronti del substrato e rallenta la velocità di corrosione finché non è completamente sciolto dai cloruri.