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RF power and $SiO_xC_yH_z$ deposition efficiency in TEOS/O_2 discharges for the corrosion protection of magnesium alloys

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Abstract

The effect of the applied voltage of 27.12 MHz TEOS/O_2/He discharges on the deposition process of $SiO_xC_yH_z$ thin films over rough as-cast Mg alloys was investigated by applying plasma diagnostics, surface characterization techniques and electrochemical impedance spectroscopy. The process efficiency in terms of power usage and deposition rate was calculated from plasma electrical and deposition rate measurements and was found to follow an inverse relation to the applied voltage, while saturating at higher voltages. Films with good substrate step coverage and free of cracks and structure failures were deposited at intermediate applied voltages and total power dissipation. As a consequence, the corrosion resistance of the films was optimized at the same conditions, indicating that in the case of no special pre-treatment of the Mg substrates, the corrosion performance is mainly determined by the $SiO_xC_yH_z$ adhesion to the substrate rather than the chemical composition of the films.
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1. Introduction

Silicon oxide like thin films deposited from organosilicon compounds have attracted particular attention the last years due to their interesting electrical, chemical and mechanical properties and their potential to be used in a variety of applications in microelectronics, food and pharmaceutical packaging and optics [1,2]. Another possible application of these materials that is recently receiving attention, envisages their use as protective coatings for increasing the corrosion resistance of metals [3,4]. For this application, plasma-enhanced chemical vapor deposition (PECVD) of $SiO_xC_yH_z$ thin films from organosilicon precursors can be used at relatively low temperatures, which is an important advantage especially for light metals like magnesium or aluminum [5]. In this direction, there is a growing number of studies dealing mainly with the effect of various plasma parameters on the structure, chemical composition and corrosion-protective properties of the deposited films [6,7]. A significantly smaller number of investigations are focused on the plasma properties and the deposition mechanisms, which is an important subject, considering the fact that PECVD of $SiO_xC_yH_z$ thin films is a rather complicated and not very well understood process.

Thus, the present work reports on the investigation of the effect of the applied voltage in 27.12 MHz TEOS/O_2/He discharges, on the deposition process of $SiO_x C_yH_z$ thin films for the corrosion protection of Mg alloys. The variation of the RF voltage and as a consequence of the RF power was chosen among the process parameters as being able to affect drastically the film growth rate as well as its chemical composition and corrosion performance [8–11]. The process was monitored using electrical measurements as plasma diagnostics and in situ film growth rate measurements. In addition, surface characterization techniques and electrochemical impedance spectroscopy were applied to evaluate the morphology, the integrity and the corrosion impedance performance of the films. The optimum results concerning the film corrosion resistance are discussed in relation to the changes in the gas phase properties.

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2. Experimental

The film depositions on 10 × 6.5 cm AZ91 and AM60 Mg alloys were performed in a capacitively coupled high-vacuum (HV) parallel plate reactor having a base vacuum of 10^{-5} Pa. The upper electrode (22 cm in diameter) is connected to the RF power generator via a matching network while the bottom grounded electrode (19.1 cm in diameter) works as substrate holder and is heated to 373 K. The distance between the two electrodes was set at 20 mm and the chamber pressure was kept constant at 0.4 mbar for this set of experiments by means of a downstream throttle valve controller. The flow rate was independently adjusted using mass flow and liquid flow controllers, respectively. Liquid TEOS is heated up to 70 °C and then transported with an O_2/He gas mixture in the reactor through the showerhead-type upper electrode, thus ensuring a uniform distribution of the reactive mixture in the discharge area.

The deposition rate was measured in situ using Laser Reflectance Interferometry [12] and the film thickness was kept at ~2 μm for all the films examined in this study. The real power consumed in the plasma as well as the discharge current and impedance were determined by using Fourier Transform Voltage and Current Waveform Measurements (FTVCW) on the RF electrode as described in detail in Ref. [13].

After sputter-coating with gold, the samples were monitored with a JSM-6300 Scanning Microscope at ×2000, ×800 and ×200 magnifications for observing the film deposition uniformity, possible cracks in the structure and failure mechanisms. In addition, the film structure and the substrate/film topography and roughness were studied by atomic force microscopy (AFM) using a commercial Multimode AFM (Nanoscope III, Digital Instruments). The system used was equipped with a piezoelectric scanner to allow a maximum scan size of 100 μm. Standard contact mode cantilevers and integrated silicon nitride tips (Digital Instruments, Santa Barbara, CA) were used. The surfaces were analyzed by measuring the average surface roughness (Ra) after a first-order flattening procedure of the height data from the 10 × 10-μm-area images.

The corrosion protective properties of the films were assessed by means of electrochemical impedance spectroscopy (EIS). Impedance measurements were carried out as a function of the immersion in an aerated 0.1 M NaCl solution, at room temperature, using a frequency response analyser EIS300 (Gamry Instruments). The impedance spectra were recorded at the open circuit potential by applying a sinusoidal signal with an amplitude of 10 mV in the $10^5 \div 10^{-2}$ Hz frequency range 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) reference electrode and a titanium counter-electrode were employed. The volume of the test solution inside the cell was 350 cm^3. The impedance data were analyzed by fitting them to a suitable equivalent circuit model described elsewhere [14,15] 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, it may be directly related to the protective properties of the film.

3. Results and discussion

Silicon oxide depositions were performed on Mg (AZ91 and AM60) alloys using TEOS/O_2/He gas mixtures at 0.4 mbar under variable 27.12 MHz power consumption in the discharge. The increase of power dissipation was induced by the variation of the RF voltage on the powered electrode while the substrates were placed on the grounded electrode. Fig. 1 summarizes the results of the electrical measurements obtained using the FTCVW technique. Namely, the discharge current (left axis) and the phase difference between voltage and current (right axis) are plotted as a function of the applied RF voltage amplitude. The values of the total power actually consumed in the discharge for each specific applied voltage are also shown as labels in Fig. 1. It is observed that the increase of the voltage is followed by an almost linear enhancement of the total discharge current and by a continuous increase of the power consumption from 7 to 77 W. This relation between current and voltage indicates that at these conditions, the discharge current is mainly due to the displacement current in the sheaths and the electron current in the bulk, the ion current being of minor importance [16]. In turn, this can be attributed to the higher frequency (27.12 MHz) that was applied in this study compared to the conventional 13.56 MHz. The use of higher frequency allows for the increase of power at relatively low applied voltages, thus favoring the energy transfer to electrons relative to the energy consumed by ions [17]. This will also have an impact on the mechanism of the deposition process because an increase of the energy transferred to electrons is normally followed by an enhancement of the rate of electron–molecule (O_2 and TEOS) dissociation collisions, an extremely required factor in the specific process in order to favor the growth of highly inorganic films [8].

On the other hand, the increase of the applied voltage up to 135 V leads to an increase of the absolute value of the phase

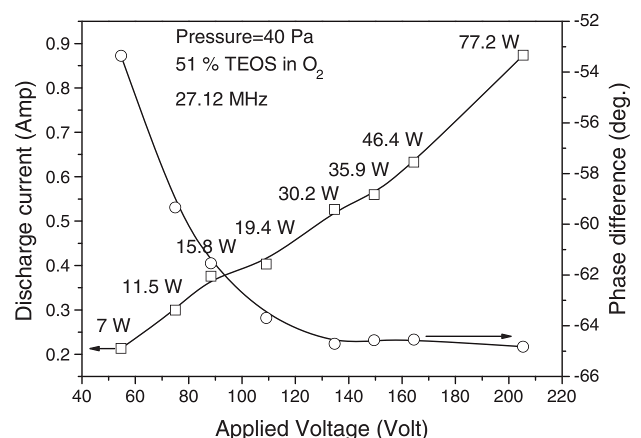

Fig. 1. Discharge current (left axis) and discharge phase impedance (right axis) as a function of the applied RF voltage for 70 Pa TEOS/O_2 discharges. The values of the real power consumed in the discharge are shown as point labels.

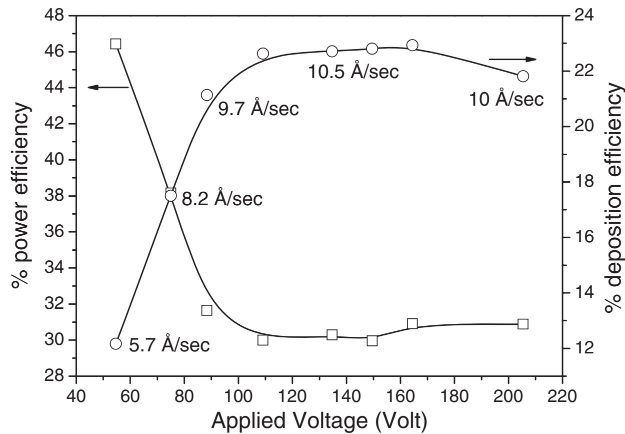

Fig. 2. % power efficiency (left axis) and % deposition efficiency (right axis) as a function of the applied RF voltage for 70 Pa TEOS/O_2 discharges. The values of the deposition rate of $SiO_xC_yH_z$ thin films are shown as point labels.

difference (right axis, Fig. 1), while a further increase of voltage does not affect the discharge impedance. The phase difference is negative over the entire range of conditions and this indicates that the electropositive character of both TEOS and He dominates over the electronegative character of O_2, the discharge being in the capacitive regime. In fact, the enhancement of the capacitive nature of the discharge at higher applied voltages can be the result of the contribution of positive ions produced by either O_2 or He ionization, as both these processes have a higher appearance threshold (13 and 24 eV, respectively [18]) compared to O_2 dissociative attachment or TEOS ionization (4.4 and 11 eV, respectively [18,19]) and will be favored by the voltage increase.

This enhancement of the capacitive character of the discharge has a definitive effect on the energy transfer efficiency from the generator to the plasma. In order to monitor this change, Fig. 2 (left axis) presents the power efficiency defined as the ratio of the real power consumed in the discharge (as obtained from Fig. 1) to the nominal (generator output) power. It is observed that, following the variation of the discharge impedance, the increase of the applied voltage up to 135 V induces an abrupt drop of the power efficiency that is stabilized at values around 30% to a further increase. The highest transfer efficiency value (46%) is obtained for the lowest applied voltage and is remarkably high compared to other depositing gas discharges [13] as well as compared to the same process operated at lower frequencies [20]. This significant advantage of the higher frequency is mainly due to the better matching of the extremely large cross sections of TEOS for low electron energy impact by the swarm produced at this frequency.

Moreover, in order to have a complete picture of the process efficiency, in the right hand axis of Fig. 2 is plotted the % deposition efficiency as a function of the applied voltage. The deposition efficiency (%DE) is defined according to the relation [21]

$$\%DE = \frac{DR \times A_{el} \times \rho}{(N_L \times X^{o}_{TEOS} \times MW_{TEOS} \times flow)/N_{Av}}. \quad (1)$$

The numerator in Eq. (1) stands for the rate $SiO_xC_yH_z$ fragments are involved in the film growth at the deposition electrode area, where DR is the deposition rate, A_{el} the deposition surface area and ρ the mass density of $SiO_xC_yH_z$. The denominator is the rate that TEOS molecules are introduced in the discharge. N_L is the Loschmidt number, X^{o}_{TEOS} the fraction of TEOS in the gas mixture in the discharge off conditions, MW_{TEOS} the molecular weight of TEOS, F the total flow of the mixture and N_{Av} the Avogadro number. This relation is based on the simplifying approximation that the reactor is of plug flow type, which, despite the low pressure used, gives a good estimation of the variation of the gas usage efficiency and the effectiveness of the process with the applied voltage. In fact, the % deposition efficiency at these specific conditions depends only on the deposition rate, with all other parameters of Eq. (1) remaining about the same. Thus, the $SiO_xC_yH_z$ film growth rates obtained with the specific applied voltages are included as point labels in Fig. 2 in order to follow the changes on the deposition efficiency. As one can observe, the increase of the applied voltage leads to a very fast rise of the % deposition efficiency from 12% to 22%. After that, the deposition rate and the % efficiency remain constant for voltages between 130 and 170 V and then drop again for the highest applied voltage.

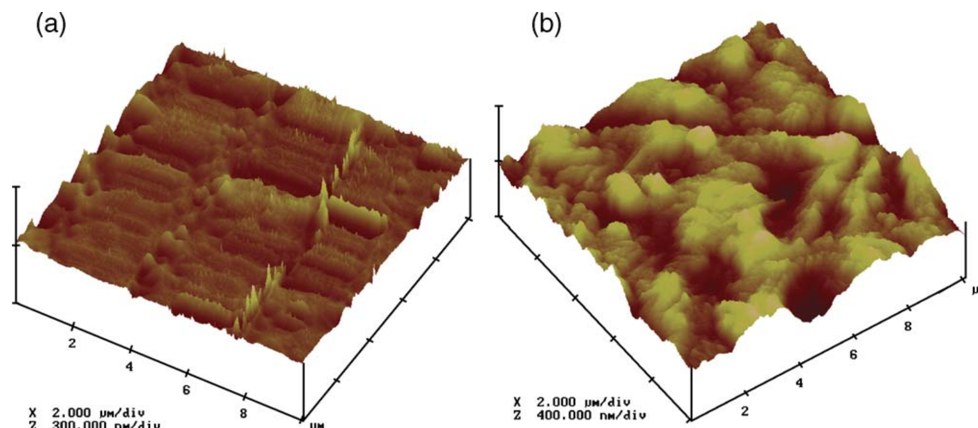

Fig. 3. (a) AFM micrograph of $SiO_xC_yH_z$ thin film deposited on Mg AM60 alloy from 51% TEOS/O_2 discharges at total pressure of 70 Pa and plasma power of 35.9 W and (b) AFM micrograph of bare Mg AM60 alloy.

The rather low % deposition efficiency values obtained (<22%) clearly show that despite the high power density and power efficiency, TEOS is either not totally consumed in the discharge or the products of the dissociation do not contribute to the film growth. In addition, the constant deposition rate and efficiency over a wide range of voltages indicate that the extra amount of power fed into the plasma does not favor gas phase processes which have a significant contribution to the film growth. The O_2 and He ionization processes that have been discussed above in order to explain the enhancement of the capacitive nature of the discharge at higher voltages can be good examples of processes that consume large amounts of electron power without favoring the film growth rate.

Furthermore, in order to follow the indirect changes produced by the increase of the applied voltage and the consequent increase of the discharge power on the deposited films structure and morphology, AFM micrographs and SEM images of $SiO_xC_yH_z$ thin films deposited on Mg alloys (AZ91 and AM60) were taken for all plasma conditions presented above. Thus, Fig. 3 includes the AFM pictures before and after the deposition of $SiO_xC_yH_z$ on the AM60 Mg alloy. It can be clearly observed (Fig. 3b) that the substrate of the bare metal is rather rough (calculated average roughness ~58 nm with standard deviation ±25 nm), while in the case of the coated sample (Fig. 3a), the surface roughness is reduced to an average value of ~17±8 nm. In the case of AZ91 alloy, the change of the surface roughness is not so strong and in the bare metal is ~29±8 nm while in the coating is ~17±9 nm. It results from both these examples that the measured roughness of the coated substrate is due to the morphology of the bare metals, whereas the deposition of $SiO_xC_yH_z$ always leads to a smoothening. It has to be mentioned that both AM60 and AZ91 alloys used in this study are as-cast and with no polishing prior to the deposition. The substrates have been just wet etched (5% HF acid) and dry etched (H_2 plasma) before the $SiO_xC_yH_z$ deposition.

In addition, Fig. 4(a) shows the SEM image of the films deposited on AZ91 at intermediate power conditions (35.9 W) and Fig. 4(b) of the film deposited again on AZ91 at the highest power conditions (77.2 W). Magnifications of ×2000, ×800 and ×200 were applied and different areas of the films were scanned in order to monitor the surface morphology and the

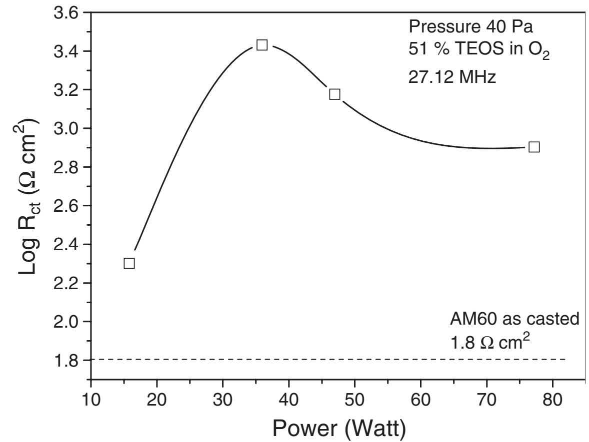

Fig. 5. Charge transfer resistance, R_{ct}, for Mg AM60 alloys coated with $SiO_xC_yH_z$ film as a function of the power dissipated in $TEOS/O_2$ discharges. The value of R_{ct} for the uncoated sample is also included.

existence of cracks in the films structures. The photographs presented in Fig. 4 are for magnifications of ×800 that corresponds to a 5×5-μm area. As one can observe, the film deposited at 35.9 W (Fig. 4a) shows very good surface step coverage and no failures in the film structure were monitored over the large area that was scanned. On the other hand, the film deposited at the highest power presents a significant number of cracks that are randomly spread over the substrate area and a typical image of these failures is presented in Fig. 4b. The differences between the two films deposited at different plasma power can be explained by the changes in the chemical composition of the films. Previous work of this group at identical deposition conditions on c-Si substrates [20] has shown that, in accordance with existing literature [8–11], the increase of the discharge power favors the growth of films with a higher inorganic character (C and OH removal). Such films can have rather high corrosion resistance but are also much stiffer preventing thus their adhesion especially in extremely rough surfaces. This is probably our case where no special pre-treatment was applied [4] or no intermediate organic layer was used to improve the adhesion [15] between the inorganic film and the rough AZ91 substrate. The same behavior was also observed for the AM60 substrates. The change of the gas phase

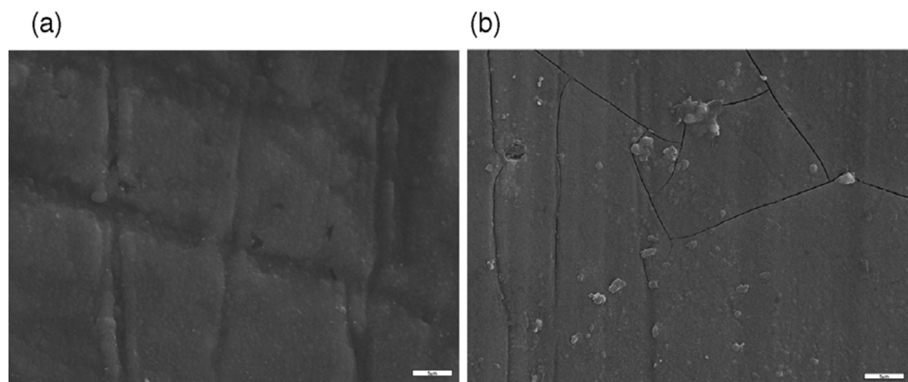

Fig. 4. SEM pictures of $SiO_xC_yH_z$ thin films deposited on Mg AZ91 alloy from 51% $TEOS/O_2$ discharges at total pressure of 70 Pa and plasma power (a) 35.9 and (b) 77.2 W.

chemistry that was predicted in the above discussion concerning the % deposition efficiency and the deposition rate may also have a role in the film failure mechanism but their relative importance cannot be estimated in this study.

Finally, the changes of the film chemical composition and adhesion are also clearly reflected on the corrosion protection of the Mg alloys. This is shown in Fig. 5 which presents the charge transfer resistance R_{ct} as measured with EIS as a function of the power dissipated in the discharge and for the films deposited on the AM60 substrate. It is observed that all the $SiO_xC_yH_z$ covered AM60 pieces show higher corrosion protection compared to the uncoated one. In addition, the increase of power results to an optimum value of the R_{ct} at an intermediate power level (35.9 W) which is probably the result of the competitive enhancement of the inorganic character of the film and the film stiffness. This result indicates that the discharge power is a very critical parameter in the optimization of $SiO_xC_yH_z$ thin films for the corrosion protection of Mg alloys, especially for the rough as-cast samples used with no special measures for the improvement of surface coverage and adhesion.

4. Conclusions

An investigation of the effect of the applied 27.12 MHz voltage of $TEOS/O_2/He$ discharges on the deposition process of $SiO_xC_yH_z$ thin films used for protecting as-cast Mg alloys against corrosion was performed.

The increase of the applied voltage was followed by an analogous enhancement of the discharge current and the power consumed in the discharge. The use of 27.12 MHz instead of the conventional 13.56 MHz excitation improves the energy transfer from the generator to the plasma allowing the achievement of rather high power densities at relatively low voltages. The energy dissipated for the acceleration of electrons was estimated to be favored in these conditions.

In addition, the increase of the applied voltage led to an enhancement of the capacitive nature of the discharge. This was attributed to the production of positive ions through a high-energy electron—O_2 and He collision processes that are favored by the voltage increase. The observed saturation or even drop of the deposition efficiency and the deposition rate at higher voltages reflects the power consumption in these processes.

The films deposited at intermediate voltages have shown very good step coverage and follow or even smoothen the rough substrate morphology of the as-cast Mg alloys. On the other hand, films deposited at high voltages present cracks randomly spread over the Mg substrates due to their highly inorganic nature and their consequent reduced flexibility and adhesion to the substrate. Similarly, the optimum values for increasing the corrosion protective properties were obtained for films deposited at intermediate RF voltages as a result of the better adhesion of these films to the Mg substrates and the partial removal of –C and –OH groups from the films. Thus, in this case, the corrosion performance is mainly determined by the $SiO_xC_yH_z$ adhesion to the substrate rather than by the chemical composition of the films.

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