XPS ANALYSES OF ZINC CONTAINING FILMS DEPOSITED BY A COLD REMOTE NITROGEN PLASMA.

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Abstract :
A method for the deposition of a zinc containing film on aluminium and polypropylene substrates by a cold remote nitrogen plasma is described. Under a contamination layer, the amounts of C and N relative to Zn in the coating are very low while oxidized zinc species are detected. Oxidation of the Zinc deposit may occur either during the process itself or during air exposure before XPS analyses. An Ar^+ etching procedure is used to progressively investigate the deeper layers.

I - Introduction

Plasma techniques know a growing interest to produce thin coating since they allow film deposition at low temperature, the thickness of the film obtained can be very low (10^{-2} - 1 µm) and the film shows a very good coverage. The formation of metal alloy films is also possible and the composition of the film can be easily controlled by variation of the flow rate of the different precursors introduced in the plasma gas [1]. Volatile hydrides or halides of some elements or organometallic compounds can be used as precursors [1-4].. The reactivity of a cold remote nitrogen plasma (CRNP) has already been used to dissociate the nickel carbonyl in order to obtain Ni deposition on an acrylonitrile-butadiene-styrene substrate [5]. In this paper, the deposition of a zinc containing film on aluminium and polypropylene substrates induced by the decomposition of diethyl zinc (DEZ) by a CRNP is described. Such films can be efficient as barriers for atmospheric corrosion and for vapor diffusion ; they also can be used to yield conductive polymer surface.

II - Experimental

1°) Samples

The deposition of zinc containing films were studied for two kinds of substrates : polypropylene (PP) provided by Goodfellow and industrial high glossy aluminium plate initially protected by an adhesive polymer film. These samples were used without previous cleaning.

2°) Film deposition procedure

The experimental set up is shown Fig. 1. A nitrogen flow (industrial quality) was excited in an electrodeless discharge by mean of a microwave generator. The transmitted power was about 400 W. The discharge was produced in a quartz tube, and, by a continuous pumping, the plasma was led to the reaction chamber. In this

chamber, the plasma denoted cold remote nitrogen plasma (CRNP) appeared like a yellow afterglow and was characterized by a very low charged particles concentration and an important thermodynamic non-equilibrium [6].
DEZ was introduced in the CRNP by mean of an injector at 45° from nitrogen flow. The injector was a pyrex tube (8 mm inner diameter) bored by nine holes spaced by 3 cm and winded as a plane spiral (7,5 cm diameter). Samples which have to be metallized were small disks (5 cm^2) settled in the reactor, parallel to the injector. The deposition process was carried out in three stages : at first, samples were treated by the CRNP for 5 minutes in order to clean the samples (degreazing effect) [7] and to increase their adhesivity in case of polymeric samples by grafting some chemical functions [8]. Then, the deposition phase (5 minutes) was performed directly after the previous pre-treatment and without air exposure. The CRNP decomposes DEZ, leading to the appearance of a blue luminescence and to the formation of a film with a blue grey metallic appearance on the sample and on the walls of the reactor. Samples were settled in the middle of the blue flame at 3 cm from the injector. The DEZ and nitrogen partial pressure were respectively equal to 0.1 and 4 hPa.

3°) Film characterization

The surface morphology of deposited film was examined by SEM using a JEOL-JSMT330 A.
The nature of the deposited species and the atomic composition of the films were characterized by XPS (LHS 10 spectrometer) with sequences of Ar^+ etching. The Al Kα X-Ray source operated at 13 kV and 20 mA current emission. The atomic stoichiometries were determined by the ratio $n_A/n_B = I_{A_i}/I_{B_j} \cdot K_{B_j}/K_{A_i}$ where $I_{A_i(B_j)}$ is the i(j) photopeak intensity of the element A(B) and $K_{A_i(B_j)}$ is the result term between the cross section of the i(j) core level orbital, the inelastic mean free path and the transmission factor of the analyser, both of the latter being kinetic energy-dependent. The efficiency of the electron detector was considered to be constant.
Before XPS analysis, samples were exposed to ambient air during about 10 minutes.

4°) Film adhesion quality

The adhesion quality was checked by the cross hatch cutter test : the deposited film was cut to the substrate as a cross hatch pattern. The adhesion quality could be quoted from the number of zones which comes unstuck under the action of a normalized adhesive tape (NFT 30038). A good adhesion is characterized by no unstuck zone.

III - Results and discussion

Results described in this paper have to take into account that the process was developed with the objective to be consistent with a prospective industrial application. So, the working conditions involved various origins of oxidation which were not eliminated (commercial nature of the samples used without previous cleaning procedure, impurities in the plasma gas and in the primary vacuum system). The air exposure of the deposited film between its production and its characterization by XPS was also an important source of oxidation. In order to elucidate the role of the different oxidation processes, XPS results were discussed versus the duration of an Ar^+ etching of the Zn containing film.

1°) Scanning electron microscopy

Fig. 2 shows SEM picture of the surface morphology of a film deposited on

polypropylene. This film was blue-grey with a metallic appearance. Its adhesion on polypropylene is quite good : the cross hatch cutter test reveals no unstuck zone. Results obtained with aluminium substrate are similar.

2°) XPS studies

a) References system

Two commercial samples were used as reference materials for calibrating Auger lines and photoelectron binding energies : a pure zinc foil from Goodfellow (purity ≥ 99.95 %) and a ZnO powder from Prolabo (purity ≥ 99.0 %).

The bulk zinc sample was etched first by Ar^+ during 30 minutes before XPS analysis. From the Zn 2p3/2 peak, it is impossible to distinguish Zn° from Zn^{2+} in ZnO which binding energies (BE) are respectively located at 1022.2 and 1022.3 eV. So, the Zn LMM Auger features were recorded as well (Fig. 3).

b) Deposition on aluminium

After the CRNP pre-traitment, the Al2p spectrum shows two components : the metallic one (BE = 72.8 eV) is less important than the Al^{3+} one (BE = 75.8 eV).

After an in situ Ar^+ etching during 30 minutes, the metallic component of the Al2p spectrum is prominent. The position of the Al^{3+} component (75.8 eV) and of O1s peak (533.1 eV) reveal the presence of OH group ($Al(OH)_3$ or AlO(OH) rather than Al_2O_3) provided by an oxygen contamination both at the surface and in the bulk.

Fig. 3 (a-h) shows the evolution of Zinc Auger spectra versus the Ar^+ etching duration (denoted by t) for film deposited on Aluminium.

For t = 0, the metallic Zinc contribution is not detected. Two main components appear at 986.9 and 1010.2 eV. Their shift by comparison with the ZnO reference is due to the superposition of $Zn(OH)_2$ and ZnO contributions. The position of these two main components varies with t : when t increases from 0 to 20 minutes, the kinetic energies (KE) shift respectively from 986.9 and 1010.2 eV to 987.4 and 1011.0 eV. These last values correspond to values obtained with ZnO reference. For t > 20 minutes, the KE shift towards lower KE and reach their initial values for t = 45 minutes. For t > 0, there is also the appearance of three new components at 991.8, 995.3 and 1015.2 eV. Their position are not dependant on t. The first could be a combination of Zn° and ZnO, but the two other clearly indicate the presence of metallic Zinc.

These evolutions show that for the film deposited on Al, the uppermost layer is essentially composed of ZnO and $Zn(OH)_2$. The contribution of $Zn(OH)_2$ decreases inside the film, but at the interface with oxided and hydroxylated aluminium, the $Zn(OH)_2$ component increases again.

The evolution of Zn Auger spectra versus t agrees with O1s spectra evolution. The parallel evolution of the integrated peaks intensities of C1s and N1s spectra versus t (Fig. 4) indicates that nitrogen is fixed with residual carbon coming from C_2H_5 group of DEZ which may be present as residual traces. Under the contamination layer, the amount of C and N relative to Zn are very low : for t = 20 mn, n_N/n_{Zn} and n_C/n_{Zn} are both equal to 0.008. For t ≥ 45 mn, N1s and C1s are no more detected. The incorporation of nitrogen during the film growth is very weak.

For etching time ranging from 5 to 20 mn, surface contamination by C and N can be neglected and the contribution of the substrate does not appear significantly (Fig. 4). So, by supposing that the whole oxygen detected is provided by the oxidized zinc, n_O/n_{Zn} atomic ratios can be estimate. Results are shown Table 1a. The value obtained for t = 20 mn is too high, probably due to the appearance of aluminium oxide and hydroxide components. The evolution of the proportion (%) of hydroxylated and of

ZnO components is obtained from the O1s photoelectron spectra which can be curve-resolved into two separate components which BE are located at 532.5 and 530.8 eV and correspond respectively to hydroxylated and to ZnO contributions.
For t ranging from 0 to 20 mn, there is about an equal contribution of the two components (50 ± 5 %), so, taking into account results shown in Table 1a, the average composition of the deposited film is then : Zn° = 55 %, ZnO = 30 %, Zn $(OH)_2 \simeq$ 15 %. For t > 20 mn, the contribution of the hydroxylated compound increase quickly due to the appearance of the aluminium hydroxyde contribution (Fig. 4).

c) Deposition on polypropylene

After the CRNP pre-traitment, modifications observed on the PP surfaces are responsible for the improved wettability and adhesion properties of this substrate [8].
A comparison between the C1s peak of untreated and treated PP samples gives evidence for the incorporation of nitrogenated and oxygenated functions which can be attributed to C≡N, C-O and O-C = O groups.n_O/n_C and n_N/n_C atomic ratios are respectively equal to 0.25 and 0.11.
Fig. 5 (a-f) shows the evolution of Zn Auger spectra versus t for film deposited on polypropylene.
For t = 0, two main peaks attributed mainly to ZnO are located at 987.3 and 1011.0 eV, and three shoulders appear at 990.5, 993.1 and 996.7 eV. Contribution of metallic Zn does not appear. The position of the two main peaks (ZnO) are not strongly modified by the ionic etching. Near the interface with the polymer the position of oxidized components are close to the value obtained with the reference ZnO spectrum. This can be attributed to a zinc film partly oxidized by air exposure but less contaminated by $Zn(OH)_2$. Hydroxylation seems to occur mainly at the uppermost top layers.
The integrated peaks intensities of N1s and C1s (Fig. 6) both decrease for $t \leq 2$ mn. For $t \geq 5$ mn, the integrated peak intensity of C1s increases strongly, giving evidence for the appearance of the substrate due to the morphology of the film, while the integrated peak intensity of N1s remains approximately constant because of the presence of nitrogen species grafted on PP surface initially exposed to the CRNP ($n_N/n_C = 0.11$ before deposition).
Nitrogen detected on film surface is provided by the CRNP post-treatment occuring after the end of DEZ injection.
For $t \geq 5$ mn, the nO/n_{Zn} atomic ratios are estimated supposing that the variation of the C1s peak is only due to the erosion of the deposited film leading carbon of the polymer more apparent. Results are shown Table 1b. The O1s photoelectron spectra can be curve-resolved into three separated components which BE located at 532.8, 531.8 and 530.4 eV correspond respectively to the contribution of oxygenated functions grafted on polypropylene, $Zn(OH)_2$ and ZnO. The evolution of these three components have been studied versus t. For t < 2 mn, $Zn(OH)_2$ and ZnO have about an equal contribution, but when t increases, $Zn(OH)_2$ decreases quickly while ZnO remains approximately constant and equal to 55% (2 < t, mn < 20). The contribution of oxygenated function grafted on polypropylene increases regularly as t increases. This contribution appears even for t = 0 as it can be experted from the slightly porous nature of the film shown Fig. 2.

IV - Conclusion.

A zinc containing film deposit is produced on PP and Al substrates by the decomposition of DEZ by a CRNP at ambient temperature.
Adhesion of the film on both substrates satisfies the cross hatch cutter test. Under a contamination layer due to a post-treatment by the CRNP, the amount of carbon and

nitrogen in the coating are very low. For both substrates, the Zn metallic contribution is not detected in the uppermost layer, mainly due to reactivity with ambient air. Oxidation inside the film layer may be due to an oxygen contamination during the process and at the interface with the underlying material. A diffusion of the surface oxygen contamination due to the porosity of the film cannot be excluded.
With the Al substrate, the deposition is a Zn - ZnO - $Zn(OH)_2$ mixture with a Zn rate equal to 55 %. With the PP substrate, $Zn(OH)_2$ appears mainly at the uppermost layers. Inside, the film is rather composed of a Zn - ZnO mixture, and the zinc rate reaches 60 %.

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	t (mn)	5	10	20	40
(a)	$\frac{nO}{nZn}$/Al	0.58	0.56	0.75	
(b)	$\frac{nO}{nZn}$/PP	0.50	0.39	0.44	0.49

Table 1 : $\frac{nO}{nZn}$ atomic ratios versus Ar^+ etching time t

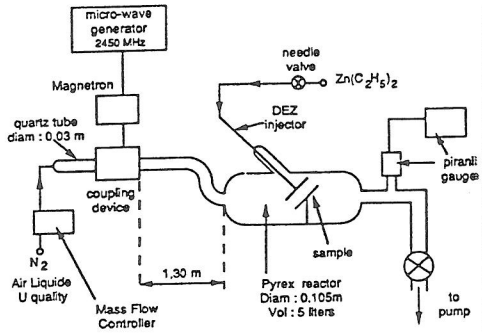

Fig. 1 : Experimental device

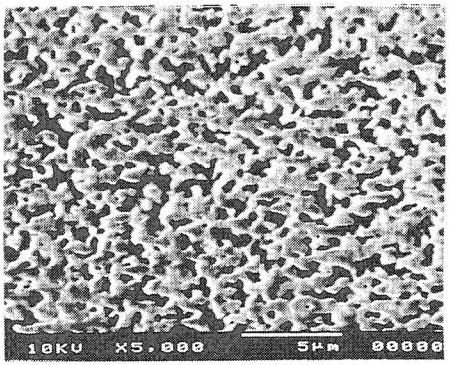

Fig. 2 : SEM picture of film deposited on PP

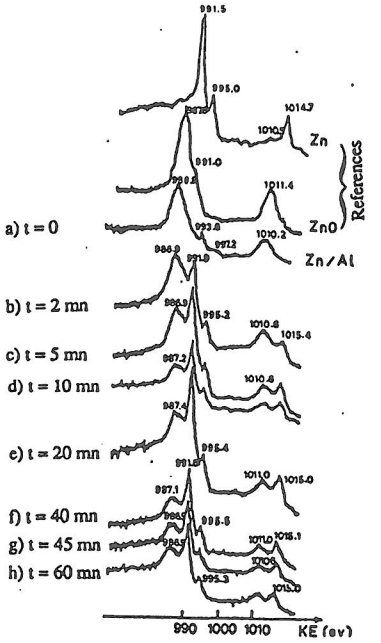

Fig. 3 : Zn LMM Auger spectra of the film deposited on Al versus t

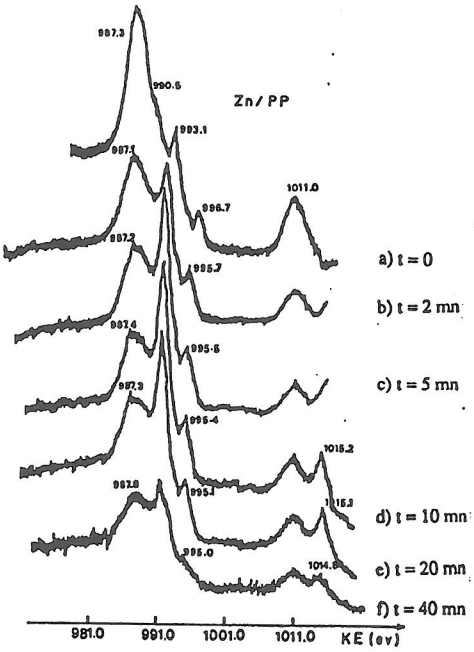

Fig. 5 : Zn LMM Auger spectra of the film deposited on PP versus t

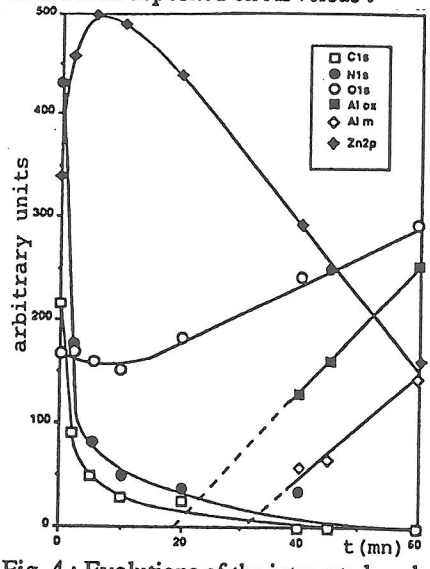

Fig. 4 : Evolutions of the integrated peaks intensities of C1s, N1s, O1s, Zn 2p3/2 and Al2p spectra versus t for the film on Al

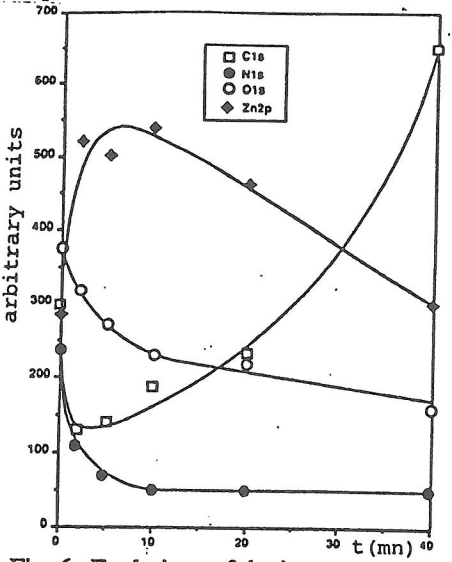

Fig. 6 : Evolutions of the integrated peaks intensities of C1s, N1s, O1s, Zn 2p3/2 Al2p spectra versus t for the film deposited on PP