Mg alloys are commonly used in various industrial sectors, especially in the automotive one because of their low weight and high mechanical strength. The main drawback of these materials is the poor corrosion resistance in atmospheric and saline environments especially caused by hydrogen corrosion. One of the most resistant, and therefore among the most investigated, of these alloys is the die-cast AZ91D. For this alloy several studies have been conducted to investigate the corrosion mechanism in saline environment. However, a complete characterization in non-aqueous environments is still missing. Such a these studies could present interesting insights on the corrosion mechanism of these alloys because of the absence of water in these environments which almost totally eliminates hydrogen corrosion. In particular, Ionic Liquids (ILs) may offer a suitable environment for this purpose.

In the last few years ionic compounds liquid at room temperature (called ionic liquids (ILs)) attracted the attention of several research groups for their interesting properties: low viscosity, non flammability, extremely low vapour pressures, high thermal stability and being liquid in a wide range of temperatures. A detailed description of the main chemical and physical properties of such class of compounds can be found in two recent reviews.

Among ionic liquids, imidazolium based ones show interesting properties in terms of low viscosity as well as thermal stability, consequently they seem to be very promising as lubricant materials, especially for aluminium containing alloys. The non-miscibility with water presented by several ILs makes them interesting materials that might to be suitable to get in contact with magnesium and magnesium alloys.

In the present work, we report on the characterization of the interaction of an imidazolium based IL and the surface of the AZ91D alloy. The ionic liquid used was composed of 1-butyl-3-methyl-imidazolium as cation and bis (trifluoromethylsulfonyl) imide as anion ([C4mim][Tf2N]). The exposure was conducted both at room temperature and at 200 °C. Our focus was on the chemical and physical monitoring of the surface evolution. To perform the study we monitored the variation of the surface average roughness by a profilograph and investigated the morphology of the sample by electron microscopy. The surface chemical composition was determined by electron dispersive X-ray (EDX) microanalysis as well as by X-ray Photoelectron Spectroscopy (XPS). Since the interaction layer formed after few days is thicker than the depth the investigated by the XPS, the method provided measurements of the elemental composition of the outermost part of the surface, while the average composition was supplied by EDX. The combined use of these techniques allowed us to differentiate the outermost part of the interaction layer from the deeper part. Moreover, XPS determines the chemical status of the elements detected and therefore monitors the evolution of the chemical species constituting the surface layer of the tested samples.

**Experimental**

The [C4mim][Tf2N] ionic liquid was synthesised in our laboratory using a similar method to that described by Dupont et al. that is starting from 1-methyl imidazole (99 %), anhydrous 1-chlorobutane (99.5 %) and lithium bis (trifluoromethylsulfonyl) imide (99.95 %) from Sigma-Aldrich and acetonitrile (98 %) from Fluka. The [C4mim][Tf2N] obtained was dried in air at reduced pressure (0.1 mbar) and slowly heated at 70 °C for 12 h to reduce the water content below 30 ppm by Karl Fisher titration.

The tested metal was a die-cast commercial magnesium-aluminium-zinc alloy AZ91D with the nominal weight composition of 90 % Mg, 9 % Al, 1 % Zn and the total amount of impurity elements (Cu, Ni, Fe, Mn, etc.) lower than 20 ppm (by ICP data). From a 12 mm diameter bar of polycrystalline alloy, several samples were prepared as thin disks (thickness less than 0.5 mm); their faces were treated with 1200 grit SiC paper, and then polished with diamond suspension of decreasing size (respectively 9, 6, 3 and 1 µm) in order to achieve a smooth and reproducible surface. The average surface roughness was measured before and after the immersion
test using a Hommel Tester W55 profilograph. The disks were weighted by an analytical balance (accuracy 0.1 mg) and arranged on a Teflon® support, placed in a Pyrex® beaker, covered with ILs and kept at constant temperature in a Carbolite furnace (model CWF 13/5). The duration of the immersion was respectively 1, 2, 4, 9, 16 and 30 days with the working temperature of 200 ± 2 °C.

After the immersion tests, the surface of the samples was cleaned by acetone (99.9 % Merck) in ultrasonic bath for 10 min, rinsing again the disks with fresh acetone, dried under nitrogen flux and then weighted again to calculate the mass loss. The surfaces were than investigated by profilometry, Scanning Electron Microscopy (SEM) and X-ray Photoelectron Spectroscopy (XPS) in order to obtain data about the morphology and the chemical composition.

The integral of the absolute value of the roughness profile height over the evaluation length (average roughness, Ra) was measured for each sample in four different points for a total length of 4.80 mm at the scan rate of 200 μm·s–1.

SEM investigations have been performed using an ISI 100B microscope equipped with an Energy Dispersive Microanalysis system (NORAN NSS 300). The acceleration voltage used was 25 kV and the take off angle was 34.7°. Quantitative data were obtained for four different spots of 0.12 mm² randomly chosen on the surfaces of every sample. The peaks acquired were fitted by Gaussian type curves applying the Proza (Phi-Rho-Z) correction method.

XPS measurements were performed in an ultra-high vacuum (10–9 mbar) system equipped with a VSW HAC 5000 hemispherical electron energy analyser and a non-monochromatized Al-Kα X-ray source (1486.6 eV). The source power was 300 W (15 kV × 20 mA) and the spectra were acquired in the constant-pass-energy mode at Epas = 44 eV. The overall energy resolution was 1.2 eV as a full-width at half maximum (FWHM) for the Ag 3 d5/2 line of a pure silver reference. Details of the system have been published elsewhere.[15]

No neutralizer was utilized and the spectra energy scale was corrected using the Mg 1 s peak (1305.0 eV). The recorded spectra were fitted using XPSPeak 4.1 software. Gauss-Lorentz curves were used to fit the data after subtraction of a Shirley-type background.

Results

Preparation and Analysis of the “Zero Point” Samples

Due to the high reactivity of magnesium and aluminium, the surface of the AZ91D alloy in air is always covered with a layer of oxides and hydroxides.[16] In order to investigate the behaviour of a real surface exposed to the ionic liquid, we decided to take as an initial “zero point” of our experiments the samples obtained after polishing without further cleaning procedure. The surface of these samples presents a thick layer of oxidation products and adventitious carbon deriving from atmospheric contamination. A survey spectrum of one of these samples is presented in Figure 1.

For these samples the weight loss was assumed to be zero and the average surface roughness was taken as an initial (zero) point.

Room Temperature Experiments

A first set of samples were placed in contact with the IL at room temperature. To avoid the effects of moisture and oxygen, a small quantity of IL was dropped, under nitrogen flux, onto the sample mounted in the XPS pre-chamber in high vacuum condition (10–7 mbar). The exposure was protracted for 3 days, after that period nitrogen was introduced in the pre-chamber to restabilize the normal pressure, and the sample was washed with acetone to remove the excess of IL. After several rinsing cycles the sample was dried and inserted in the analysis chamber to carry out the XPS measurements. No appreciable differences were detected between these XPS spectra and the one showed in Figure 1. At the same time we did not observe any change about the roughness or weight of these samples. Therefore, the reactivity of [C4mim][Tf2N] with the AZ91D alloy is negligible at room temperature.

Experiments at 200 °C

A second series of samples was placed in contact with the IL and kept at 200 ± 2 °C for up to 30 days in air. Before the immersion test, the IL was colourless and perfectly clear. During these tests at 200 °C, the colour gradually changed to brownish, becoming progressively darker with exposure. At the end of the experiment, the colour of the IL was dark brown, but no solid particle were presents as suspended corpuscles or deposited on the bottom of the beaker. The metal disks showed no apparent modification for up to 9 days of exposure. After that period a darkening of the surface became clearly detectable by visual examination. A comparison of
these results with literature data\cite{3} shows that the corrosion rate in [C₄mim][Tf₂N] is several order of magnitude lower than in standard saline solution tests. Furthermore, the samples up to 9 days are characterized by a mass loss, whereas for longer exposures the samples increased in weight (Fig. 2).

The profilometric measurements confirm this trend showing a constant increase of the average roughness from about 1.000 μm for the “zero point” samples to ca. 1.350 μm for the sample exposed for 9 days. For longer times of exposure, a slight decrease in the average roughness was observed (1.100 μm) for the samples at 16 and 30 days. The morphological investigation performed by SEM showed no difference between the “zero point” samples and the samples exposed to the IL up to 9 days. This is a remarkable difference with the tests in saline aqueous solution, where literature data\cite{2,3} report diffuse corrosion phenomena after just a few minutes of exposure. However, for the 16 days and especially for the 30 days samples, even though diffuse corrosion phenomena are still not detectable, a number of crevice corrosion spots appear on the surface (Fig. 3).

According to the literature\cite{2,17} the die cast alloy is constituted by two phases; grains of β phase (Mg₂Al₁₁) distributed in a nearly continuous matrix of α phase. In the samples exposed to saline solutions, the corrosion features appear to be originated from the β phase grains and the surrounding α phase acts as an active cathode resulting in a deep corrosion of the grains.\cite{16} In the samples exposed to the IL the density of corrosion spots is very low (1 ÷ 5 cm⁻²), so only a minimal fraction of the β phase grains presents on the surface is involved in the corrosion process. The reasons of this behaviour are still unknown. We believe that the presence of impurities may play an active role in the process, but we could not detect any composition difference between the inside of the pit and the undamaged part of the sample. According to the EDX data, the surface was composed by carbon, nitrogen and fluorine at the same side of oxygen and the main metals constituting the alloy. The quantity of the metals, especially the magnesium, significantly decrease with the time of exposure while, among the non-metallic elements, the carbon exhibits a rapid increase. These data are summarized in Figure 4.

The XPS data (Fig. 5) confirmed the EDX results: no other elements were detected on the surfaces of any of the investigated samples.

**Discussion**

In our previous work\cite{18} we used Secondary Ion Mass Spectroscopy (SIMS) to demonstrate how the interaction layer formed onto metals put in contact with [C₄mim][Tf₂N] at high temperature becomes very thick (more than 500 nm) in just a few days. In the present study we focussed on a magnesium alloy, which seems to be the most complex case among those studied so far. Here, XPS becomes a crucial technique for the understanding of the surface behaviour, since it pro-

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**Fig. 2.** Weight change (%) for the sample after the immersion test in [C₄mim][Tf₂N] at 200 °C.

**Fig. 3.** Evidence of crevice corrosion onto the surface of AZ91D. These features start to be presents after 16 days of immersion test in [C₄mim][Tf₂N] at 200 °C and became evident for the 30-days sample.

**Fig. 4.** Composition (atomic %) of the sample surface after the immersion test in [C₄mim][Tf₂N] as determined by EDX analysis.
vides accurate information about the outermost part of the interaction layer. To avoid incorrect XPS quantification, we evaluated only the concentration trends by calculating the area of the characteristic peaks and monitoring its relative contribution to the total peaks area summed for all the elements detected. The results reveal how the outermost part of the interaction layer is constituted, in addition to carbon and oxygen, by relevant amounts of fluorine, nitrogen and sulphur. On the contrary, the presence of magnesium and aluminium is largely reduced respect to the EDX data. The trend of the relative areas of the elements detected by XPS versus the time of exposure (Figs. 6 and 7) is in general agreement with the data obtained by EDX. As previously observed, carbon and nitrogen are characterized by a rapid and intense increase while the areas relative to the metals drastically decrease confirming the supposition of depletion of these elements in the outermost part of the layer. A clear disagreement between XPS and EDX can be observed for the case of fluorine. The XPS signal of this element is intense in all the samples, even if it shows a slight decreasing trend with the time of exposure (Fig. 6). On the contrary, the EDX results display a very low concentration (close to the detectability level) almost constant for all the samples (Fig. 4).

An explanation for this different behaviour of fluorine can be found observing the change of the binding energy (BE) value for this XPS peak (Fig. 8). All the samples treated at 200 °C show the presence of at least a peak attributable to this element. For the samples obtained after 1 and 2 days of exposure, a sharp and well resolved peak is clearly detectable at the binding energy of 685.7 eV. This value is consistent with the fluorine of magnesium fluoride, as reported in literature.[19]
The samples obtained after longer exposure are characterized by the presence of a new peak that becomes dominant for the 16- and 30-days samples. This peak appears at an higher energy value (BE = 688.5 eV) consistent with the fluorine in bis(trifluoromethylsulfonyl) imide molecule as demonstrated in our previous work. Therefore, we believe that the surface of the sample becomes very reactive to the IL, promoting the decomposition of the anionic part to form magnesium fluoride that in these conditions seems to be the most stable compound. This process is likely to be the reason of the enrichment of magnesium fluoride at the surface. After a few days, however, also the cationic part of the IL starts to decompose and produces a series of products that adsorb onto the solid surface. We believe that these compounds derive from the degradation of the imidazolic group, as suggested by the darkening of the solution. The new molecules so formed adsorb onto the surface, causing an increase in the thickness of the layer and therefore shielding the signal coming from the innermost part. Probably, molecules of bis(trifluoromethylsulfonyl) imide are embedded in the organic layer becoming the sources of the peak at higher binding energy. This interpretation is supported by the examination of the carbon 1 s core level transaction. The peak has a broad strongly asymmetric form, surely due to several contributions that do not allow an unambiguous deconvolution in Figure 9.

However, for the samples obtained after 16 and 30 days of exposure, a new small peak became clearly detectable near the main one. This peak is characterized by an energy (BE = 292.7 eV) almost 8 eV higher than the main one. The BE value for the 2 p core transition (not reported here) can be fitted with two components due to the contribution of 2 p1/2 and 2 p3/2, respectively. The BE value for the 2 p3/2 transition is 168.7 eV, in agreement with the value for sulphur in [Tf2N].

XPS peaks attributable to magnesium and aluminium are present in all the samples. The relative concentration of these elements progressively decreases as a function of the time of exposure. As in the case of the fluorine, this behaviour can be put in correlation with the increase of the interaction layer via adsorption of organic molecules due to the IL decomposition. The XPS signals for aluminium and magnesium, however, never completely disappears, even when the thickness of the corrosion layer became several times larger than the depth of analysis of XPS (normally 6-8 nm for organic substances). This result can be explained in terms of roughness of the surface and to diffusion processes inside the interaction layer.

A summary of the peaks detected in the XPS spectra and their attribution is shown in Table 1, the uncertainty in the BE value reported is due to the slight differences presents in the samples, probably due to the charging effect.

The combination of the XPS and EDX results reveal how temperature plays a key role in the formation of the interaction layer. At 200 °C at least two different mechanisms take place. The first dominates the initial phase of corrosion and consists in the oxidation of the metallic elements constituting the alloy. This process actively contributes to the formation of different oxidation products.
increase of the surface roughness and the weight loss observed. During this phase, the interaction layer is mainly constituted of alloy oxidation by-products, such as metals oxides and fluorides. The presence of water and oxygen dissolved in [C₄mim][Tf₂N] is not negligible even at 200 °C[22] and this is probably the source of the oxygen detected on the surface while the fluorine was provided by the [C₄mim][Tf₂N] itself. After a few days, a second mechanism takes over in determining the composition of the interaction layer: the adsorption of the decomposition products of the cationic part of the IL. As a consequence, the interaction layer results enriched in organic compounds, the average roughness decrease and an appreciable increase of weight is detected. The IL decomposition process is probably catalysed by the metals constituting the alloy.[23] This interpretation is confirmed by differential calorimetry studies[24,25] which indicate that [C₄mim][Tf₂N] is stable up to temperature much higher (about 400 °C) than the used in our experiments.

Conclusion

The results of the present study provide a detailed characterization of the surface of the AZ91D alloy after that it has interacted with 1-butyl-3-methylimidazolium bis (trifluoromethylsulfonyl) imide ([C₄mim][Tf₂N]). In general, we observed that the corrosion rate is relatively slow, especially at room temperature. It becomes fast at higher temperatures (200 °C). At least two different processes contribute to the formation of the interaction layer. The first is the corrosion of the metals constituting the alloy with the formation of oxides and fluorides. The second mechanism activates after few days of exposure and quickly becomes dominant; the adsorption of [C₄mim][Tf₂N] degradation products onto the surface. This process starts after 9 days of exposure and it causes the rapid increase in the thickness of the interaction layer. The layer is mainly composed by carbon, nitrogen and fluorine and it appears to be quite homogeneous.

These results reveal how temperature plays a key role in the formation of the interaction layer. At the same time, we found that the decomposition of the IL in the presence of the AZ91D alloy starts at temperatures much lower than for the IL alone, therefore a catalytic role of the metals in the decomposition process appears to be at work. The formation of the organic interaction layer contributes to stop the extended corrosion process, but the alloy oxidation continues, even though at a much lower rate, via crevice corrosion phenomena. Probably, the oxygen and/or water dissolved in the [C₄mim][Tf₂N] are enough, at 200 °C, to promote the alloy oxidation. Further studies, concerning the effect of oxygen and water content on the corrosion phenomena are currently under examination and will be the object of a future publication.

Received: October 04, 2006
Final version: October 16, 2006