Surface modification of industrial alloys induced by long-term interaction with an ionic liquid

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The surface modification of Inconel 600, Naval Brass and AISI 1018 carbon steel after immersion into the [C4mim][Tf2N] ionic liquid (IL) at 225°C for 20 days has been studied using SIMS, XPS and by surface topography measurements. The trace concentration of alloys’ components in the IL solution after the immersion test was measured by inductively coupled plasma-optical emission spectroscopy (ICP-OES). Appreciable amounts of carbon, nitrogen, oxygen, sulphur and fluorine were detected on the surface of the alloys after the immersion test because of thermal decomposition of the IL. The corrosion layer formed onto the surface of Inconel was found to be rather thick (ca 400–500 nm) and rough (Ra ≈ 100–200 nm) due to the dominant adsorption of the IL decomposition products. At the same time, Inconel exhibited minor weight loss (2.5 × 10⁻⁵ g cm⁻²) after the immersion test. On the contrary, for Brass, the thickness (70–100 nm) and roughness (Ra ≈ 80–100 nm) of the corrosion layer were the smallest among the alloys studied, and the weight loss was the greatest (1.3 × 10⁻² g cm⁻²). It is assumed that IL decomposition might be catalysed by some metallic atoms, for instance Ni, that, in turn, could slow down the surface corrosion and migration of metal atoms into the ionic liquid. Copyright © 2006 John Wiley & Sons, Ltd.

KEYWORDS: corrosion; inductively coupled plasma-optical emission spectroscopy; ionic liquid; metal alloy; secondary ion mass spectrometry; X-ray photoelectron spectroscopy

INTRODUCTION

Ionic liquids (ILs) at room temperature are essentially salt-like materials composed of organic cations combined with organic or inorganic anions.1 Their distinctive features are the high thermal and chemical stability, heat capacity and ability to retain the liquid state over a wide temperature range with negligible vapour pressure. ILs are used as solvents for clean (‘green’) chemical synthesis and catalytic processes, and as electrolytes in electrochemical devices.2,3 Recently, their application as working fluids for heat transfer has been considered with encouraging results.4 However, the understanding of the interaction between ILs and materials employed in the construction of thermal storage and exchange devices in chemical reactors is still at a very early stage.

In the present work, we report about a study of the surface modification of different industrial metal alloys after long-term interaction with an IL composed of 1-butyl-3-methylimidazolium as cation and bis(trifluoromethane)sulfonimide as anion ([C4mim][Tf2N]). Our focus is on the elemental depth profiling by SIMS and surface chemical identification by XPS, and on the measurements of the surface topography of the alloys by a stylus profiler. The trace concentration of the alloys’ components in the IL solution after immersion test was measured by inductively coupled plasma-optical emission spectroscopy (ICP-OES).

EXPERIMENTAL

The tested materials were polycrystalline Inconel 600 (wt%, Cr 15.5, Fe 8, Mn < 1, Cu, Si, C, S < 0.5 total, Ni balance) and Naval Brass (wt%, Zn 36.7 to 40.2, Sn 0.5 to 1, Fe, Pb < 0.5 total, Cu balance) from Goodfellow, and carbon steel AISI 1018 (wt%, C 0.14 to 0.2, Mn 0.6 to 0.9, P, S < 0.1 total, Fe balance) for an industrial application.

The IL (Fig. 1) was synthesised in our laboratory in a similar way as described in5 starting from 1-methyl imidazolone (99%), anhydrous 1-chlorobutane (99.5%) and lithium trifluoromethane-sulfonimide (99.95%) from Sigma-Aldrich and acetonitrile (98%) from Fluka. The [C4mim][Tf2N] obtained was dried in air at a reduced pressure of 0.1 mbar and gently heated at 70°C for 12 h to reduce the water content below 300 ppm by Karl Fisher titration.

The tested materials were immersed into IL and placed in a Carbolite furnace (model CWF 13/5) at 225°C for 20 days. At the end of the test, the samples were cleaned with acetone (99.9% Merck) in ultrasonic bath for 15 min and then rinsed again with acetone.

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The SIMS measurements were carried out with a multifunctional custom-built installation at IENI-CNR, Padua. The details of the system have been reported in our previous publication.\textsuperscript{7}

The depth of the sputtered craters and the surface topography were determined with a Tencor Stylus Profiler P-10. Roughness measurements were made from three different areas of $600 \times 600 \mu m^2$ each, randomly chosen on the surface of the samples. The scanning velocity was $50–100 \mu m/s$ and the total amount of lines per image was 100.

XPS measurements were performed in an experimental high-vacuum ($10^{-9}$ mbar) system equipped with a VSW HAC 5000 hemispherical electron energy analyser and a non-monochromatic Al-K\textsubscript{x}, X-ray source (1486.6 eV). The details of the system have been published elsewhere.\textsuperscript{6} The experimental spectra were fitted using mixed Gaussian–Lorentzian curves and Shirley-type background was subtracted.

ICP-OES measurements were carried out with a standard Perkin Elmer Optima 2000 DV spectrometer. We analysed ca 100 mg of the IL solution after immersion test for every alloy using a standard analytical protocol.\textsuperscript{8}

### RESULTS AND DISCUSSION

The 20-day immersion test resulted in the formation of an inhomogeneous dark-brown-colour layer on the sample surface whose thickness and roughness depended on the alloy. For instance, an originally smooth surface of Inconel exhibited a sevenfold rise in the average roughness, $R_a$, which amounted to 200–250 nm. On the contrary, roughness of the Brass and the AISI samples increased insignificantly; its value ranged between 70–120 nm.

After the immersion test, IL turned dark. The solution that had reacted with Inconel was the darkest, and that for the Brass sample was the clearest. The change in the colouration is the evidence of the IL decomposition, and such process was the most pronounced for the Inconel sample. At the same time, as was revealed by ICP-OES, the solution after interaction with Inconel contained only little amount of Ni, but Cr was not detected (Table 1). We estimated the weight loss of the tested alloys in g x cm$^{-2}$ as $2.5 \times 10^{-3}$ for Inconel, $1.3 \times 10^{-2}$ for Naval Brass and $2.0 \times 10^{-2}$ for AISI steel.

Metal corrosion and decomposition of ILs can be considered as the most relevant processes, which contribute to the surface modification of alloys. It is known\textsuperscript{9} that when metal surfaces come into contact with electrolytes, metal atoms migrate into solution as positively charged ions. At the same time, dissolved oxidants such as oxygen, halogens and molecules of water are absorbed by metal surface and cause its corrosion. Under equilibrium conditions, the rate of diffusion of metal atoms is equal to the rate of oxidants moving towards the metal surface. With regard to the second process, the mechanism of the IL decomposition on the metal surface is not presently clear; however, a catalytic effect of metals, especially Ni, could be assumed. Dimerisation and dealkylation of some imidazolium-based ILs are described in the literature;\textsuperscript{10} however, it is shown\textsuperscript{11} that they are carbonised, particularly, if heating is performed in the air. IL decomposition products such as the imidazolium ring (C=N), (–CF$_3$) and (–SO$_2$–) and their components (C, N, O, F, S) could adsorb onto the metal surface and slow down or even inhibit surface corrosion and migration of metal atoms into the solution.

Figure 2 shows a mass spectrum of the negatively charged secondary ions measured for the Inconel sample after the immersion test. The negative ions were found to be most informative in representing the components of both the IL and the alloys. The spectrum includes different types of secondary ion species and appears very complex. The proper interpretation of such spectra is an intricate problem, especially for quadrupole-based SIMS. Our approach to solving this problem is discussed in detail elsewhere.\textsuperscript{12}

The results of the mass spectra decomposition by DECO computer code are shown in Table 2, where the intensity for every species represents the sum of all isotope ions. The spectrum is dominated to a great extent by the peaks relevant to the IL decomposition products yielding atomic

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Inconel 600</th>
<th>Naval Brass</th>
<th>AISI 1018</th>
</tr>
</thead>
<tbody>
<tr>
<td>Component</td>
<td>Ni</td>
<td>Cr</td>
<td>Cu</td>
</tr>
<tr>
<td>Concentration</td>
<td>$8.7 \times 10^{-3}$</td>
<td>Undetected</td>
<td>2.7</td>
</tr>
</tbody>
</table>

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{inconel}
\caption{Inconel.}
\end{figure}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{mass_spectrum}
\caption{Mass spectrum of the negatively charged secondary ions measured for the Inconel sample after the immersion test. Experimental conditions: 6 keV $^{16}$O$_2^-$ primary ions, 50% electronic gate, 0.2 mm$^2$ sputter area.}
\end{figure}
CH14.4 NiO3 0.3
CF16 FeOH 0.4
CaOH2 17.3 CaF 0.45
where the intensity of the particular molecular ion involving
oxide–metal interface, therefore the region of the profile,
as primary ions. For this reason, we could not monitor the
depth distribution is not shown here since we used oxygen
ions representing the alloys' components. The oxygen in-
for the IL decomposition products, and some intense cluster
negatively charged ions C
gate' was reduced as well. We monitored the signals of the
quality of the in-depth analysis, the energy of the primary
immersion test are shown in Fig. 3(a)–(c). To improve the

Table 2. Identification of the main negatively charged
secondary ions measured for the Inconel sample (Fig. 2). The
sum total of the peak intensities is 3.982 × 10^6 cps, and the
unidentified remainder is 2.23 × 10^5 cps (5.6%)

<table>
<thead>
<tr>
<th>Ion species</th>
<th>Intensity (x10^3 cps)</th>
<th>Intensity (x10^3 cps)</th>
</tr>
</thead>
<tbody>
<tr>
<td>F</td>
<td>2160</td>
<td>C4H2O</td>
</tr>
<tr>
<td>C4H2</td>
<td>1130</td>
<td>CaHF</td>
</tr>
<tr>
<td>C2</td>
<td>239</td>
<td>SOH</td>
</tr>
<tr>
<td>O</td>
<td>72.7</td>
<td>SH</td>
</tr>
<tr>
<td>C</td>
<td>66.7</td>
<td>SO2</td>
</tr>
<tr>
<td>S</td>
<td>58</td>
<td>CH2</td>
</tr>
<tr>
<td>Cl</td>
<td>42.2</td>
<td>O2</td>
</tr>
<tr>
<td>C2H</td>
<td>28.5</td>
<td>FeO</td>
</tr>
<tr>
<td>SO</td>
<td>27.9</td>
<td>Cr2O3</td>
</tr>
<tr>
<td>HCl</td>
<td>26.8</td>
<td>SO3</td>
</tr>
<tr>
<td>CF2</td>
<td>26.6</td>
<td>CrO</td>
</tr>
<tr>
<td>CaOH2</td>
<td>17.3</td>
<td>CaF</td>
</tr>
<tr>
<td>CF</td>
<td>16</td>
<td>FeOH</td>
</tr>
<tr>
<td>CH</td>
<td>14.4</td>
<td>NiO3</td>
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<tr>
<td>OH</td>
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<td>CaHF2</td>
</tr>
<tr>
<td>CHF2</td>
<td>7.2</td>
<td>CrO2</td>
</tr>
<tr>
<td>H2Cl2</td>
<td>6.13</td>
<td>NiO2</td>
</tr>
<tr>
<td>CaO</td>
<td>5.9</td>
<td>FeO2</td>
</tr>
<tr>
<td>H2C2O4</td>
<td>5.6</td>
<td></td>
</tr>
</tbody>
</table>

and various oxygen-containing molecular (cluster) ions. Both
positive and negative SIMS mass spectra measured for the
Brass and the AISI samples exhibit similar complex character.
The SIMS depth profiles of the samples subjected to the
immersion test are shown in Fig. 3(a)–(c). To improve the
quality of the in-depth analysis, the energy of the primary
ions was decreased by a factor of 2 as compared to that
used for the acquisition of mass spectra, and the 'electronic
gate' was reduced as well. We monitored the signals of the
negatively charged ions C−, F− and (CH2)− as characteristics
for the IL decomposition products, and some intense cluster
ions representing the alloys' components. The oxygen in-
depth distribution is not shown here since we used oxygen
as primary ions. For this reason, we could not monitor the
oxide–metal interface, therefore the region of the profile,
where the intensity of the particular molecular ion involving
an atom of the major component of the alloy (e.g. NiOH2−,
CuOH−, ZnO−, FeF−) reaches a maximum level (Fig. 3),
was considered as the boundary of the corrosion layer.
In the framework of this approach, the thickness of the
corrosion layer was roughly estimated within the range of
400–500 nm for the Inconel, 75–100 nm for the Brass and
ca 250–300 nm for the AISI samples. The sputter time was
converted into eroded depth by assuming a constant erosion
rate $V = 20 ± 5$ nm/min. For every sample studied, the
interlayer boundary was found to be smeared because of
non-homogeneity and roughness of the corrosion layer.
The results of identification of the surface chemical and
phase composition derived from XPS data are given in
Table 3. For all the materials subjected to the immersion
test, appreciable amounts of carbon, nitrogen, oxygen and
fluorine are detected on the surface. The interaction of Inconel
with the IL, results in such modification of the surface that
is accompanied by a strong suppression of the peaks related
to photoelectron emission from Ni; at the same time the Cr
peaks experience little change. This implies that the corrosion
layer formed is thick enough in comparison with the mean
free path of the Ni 3p photoelectrons with the kinetic energy
$E_{Ni 3p} \approx 1420$ eV and contains nickel in small quantities, if
any. On the contrary, chromium is rather abundant in
the products of corrosion. According to the ICP-OES data
(Table 1), Cr was not detected in the IL after the immersion
test while some trace amount of Ni was measured. This
implies that Ni atoms actively migrate into the solution and
stimulate IL decomposition process.

Similar selectivity in corrosion of different components
of the alloys is also observed for Brass. Indeed, while copper
is hardly detectable at the surface after the corrosion test
($E_{Cu 3p} \approx 1410$ eV), the intensity of zinc in the products is
nearly the same as in the original alloy. At the same time, Cu
content in the IL after the immersion test was found to be
about 50% more than that of Zn (Table 1).

During the XPS analysis, the treated samples exhibited
surface charging effects. Since adventitious carbon was
always present, the C 1s peak with the binding energy
$BE = 284.8$ eV was used as a reference for the correction
of the surface charging. The C 1s intensity increased after
the immersion test in comparison with the original state
due to the contribution of aliphatic carbon from the IL
decomposition products. Besides the shift of the binding
ergies, the induced broadening of the core lines was
detected that did not allow any further peak deconvolution.

Table 3. XPS data: Surface chemical and phase composition of the samples after the corrosion test

<table>
<thead>
<tr>
<th>Element</th>
<th>Line</th>
<th>BE (eV)</th>
<th>Attribution</th>
<th>BE (eV)</th>
<th>Attribution</th>
<th>BE (eV)</th>
<th>Attribution</th>
</tr>
</thead>
<tbody>
<tr>
<td>F</td>
<td>F 1s</td>
<td>688</td>
<td>–CF4</td>
<td>688</td>
<td>–CF3</td>
<td>688</td>
<td>–CF3</td>
</tr>
<tr>
<td>O</td>
<td>O 1s</td>
<td>532</td>
<td>NiO2</td>
<td>533</td>
<td>CuO3/CuO2</td>
<td>530</td>
<td>Fe2O3</td>
</tr>
<tr>
<td>C</td>
<td>C 1s</td>
<td>286</td>
<td>C = N</td>
<td>286</td>
<td>C = N</td>
<td>286</td>
<td>C = N</td>
</tr>
<tr>
<td>Ni</td>
<td>Ni 2p3/2</td>
<td>855</td>
<td>NiO2</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>Cu</td>
<td>Cu 2p3/2</td>
<td>–</td>
<td>–</td>
<td>934</td>
<td>CuO3/CuO2</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>Zn</td>
<td>Zn 2p3/2</td>
<td>–</td>
<td>–</td>
<td>1022</td>
<td>ZnO2</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>Fe</td>
<td>Fe 2p3/2</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>711</td>
<td>Fe2O3</td>
</tr>
</tbody>
</table>
The results of the present study provide a detailed characterisation of the corrosion layer formed on the surface of Inconel, Naval Brass and AISI 1018 carbon steel after long-term interaction with the [C<sub>4</sub> mim][Tf<sub>2</sub> N] IL. In general, we observed rapid and intense surface modification of all the materials studied due to corrosion and adsorption of the IL decomposition products. The dark-brown-colour corrosion layer was found to be thick, for instance up to 400–500 nm for Inconel, and rough ($R_a \approx 100–200$ nm) with some inhomogeneities and pits. Appreciable amounts of carbon, nitrogen, oxygen, sulphur, and especially fluorine were detected by SIMS and XPS on the surface after the immersion test. These elements, in the different chemical and phase states, originated mainly from the IL decomposition products.

According to ICP-OES, Inconel exhibited minor weight loss after the immersion test. At the same time, the corrosion layer formed on the surface of Inconel was very thick and rough due to the dominating adsorption of the IL decomposition products. On the contrary, for Brass, the thickness and roughness of the corrosion layer were the lowest among the alloys studied, while the weight loss was the largest. It implies that intense IL decomposition could slow down surface corrosion and migration of metal atoms into the electrolyte, and some metallic atoms, Ni for instance, might catalyse the IL decomposition. However, the use of ILs as working fluids in high-temperature chemical reactors requires additional investigations aimed at clear understanding of the interplay of corrosion and decomposition processes.

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