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Effect of Ionic Liquids with Imidazolium and Lactam-Based Cations on Corrosion of Mild Steel

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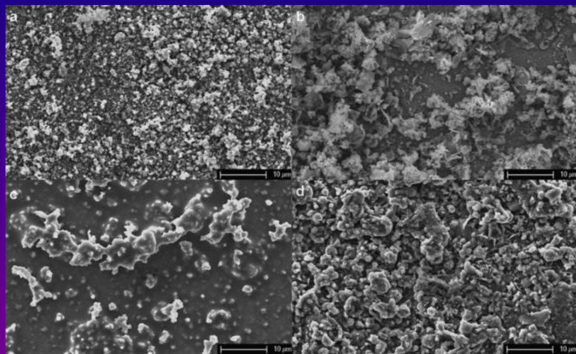
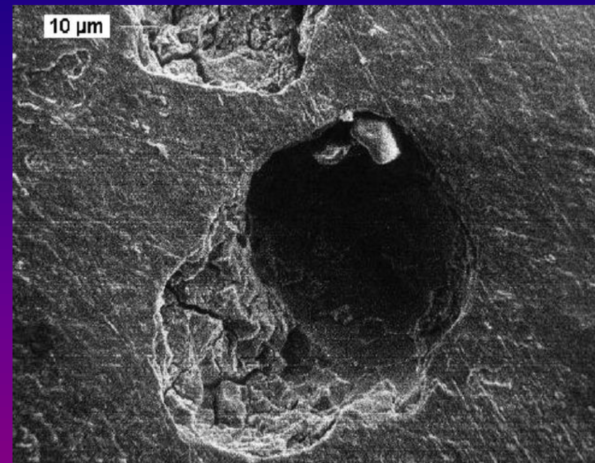
Examples of corrosion in ILs



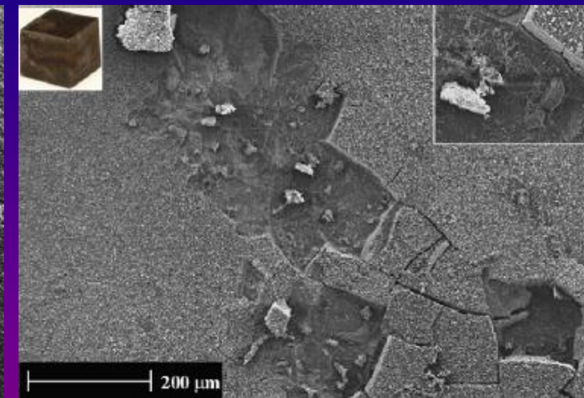
SEM images of the iron oxide layers formed on the 100Cr6 steel surfaces after immersion in various ILs [C. Gabler et al., Green Chem. 13 (2011) 2869]

SEM micrograph of AA 2011 Al alloy after immersion in IL at room temperature for 30 days [M.-D. Bermudez, Appl. Surf. Sci. 253 (2007) 7295]



SEM image showing pitting feature of AISI 1018 after 48 h immersion at 275 °C in [C_4mim][Tf2N] [I. Perissi et al., Corros. Sci. 48 (2006) 2349]

SEM micrograph of mild steel electrode after potentiostatic anodic polarisation for 1 h in EMI–DCA IL [Y.-C. Wang et al., Corros. Sci. 78 (2014) 81]



SEM image of 100Cr6 immersed in IL containing 1.5% of water [L. Pisarova, Tribol. Int. 46 (2012) 73]

Corrosion on AISI52100 disc specimen after sliding against AISI52100 ball with [PP13][TFSI] at 50 °C for 12 h [Y. Kondo, J. Eng. Tribol. 226 (2012) 991]

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Outline of the presentation

Two types of degradation of mild steel (MS) in ionic liquids (IL)

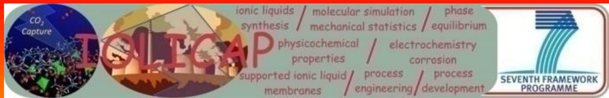
Local changes on the surface at the locations of MnS inclusions present in the steel

Modification over the macroscopic surface of the alloy

MnS inclusion-induced corrosion in the ILs with imidazolium-based cations

Selective etching in the IL with lactam-based cation

Application of molybdate inhibitor to the IL with lactam-based cation



Materials

Mild steel:

0.13-0.18 % C, max. 0.40 % Si, 0.7-0.9 % Mn, max. 0.05 % S, max. 0.05 % P and Fe balance.

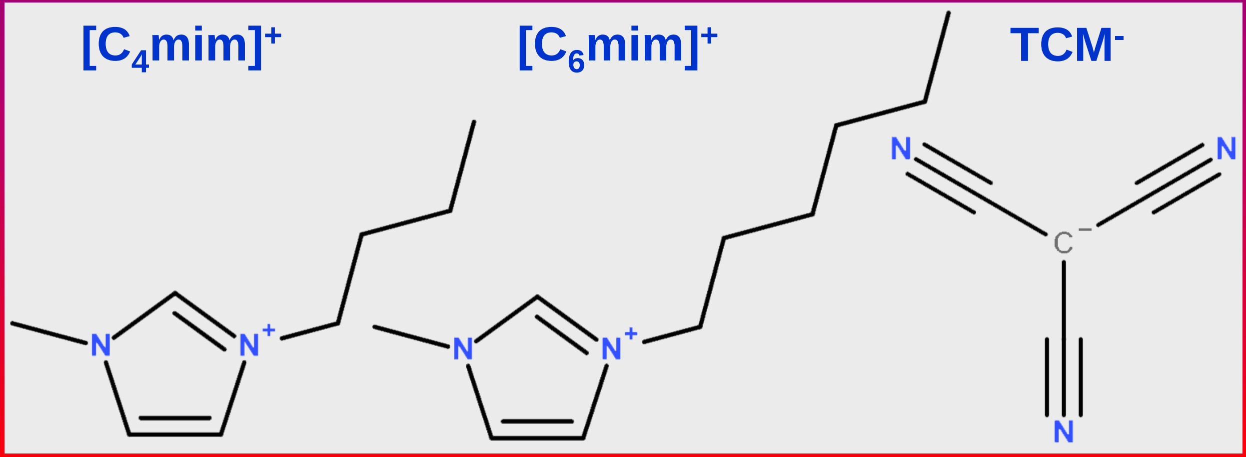
An important structural material that is used for building many metallic products.

Combines relatively high strength and low cost.

Prone to corrosion and proper measures should be undertaken for protection of the alloy in operating environment.

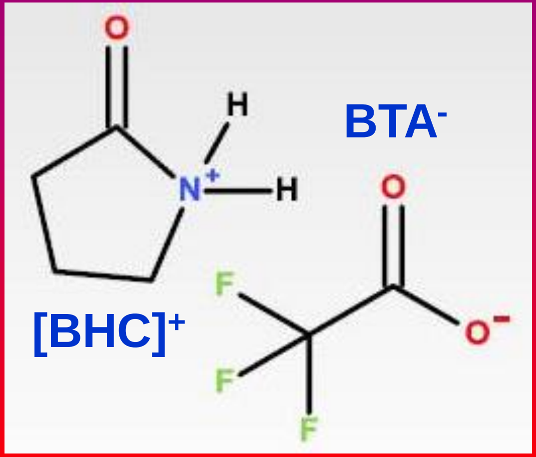
Ionic liquids designed for CO_2 capture applications:

with imidazolium-based cations



1-butyl-3-methylimidazolium tricyanomethanide, $[C_4mim]TCM$,
1-hexyl-3-methylimidazolium tricyanomethanide, $[C_6mim]TCM$

with lactam-based cation



Pyrrolidium-2-one bis[(trifluoromethyl)sulfonyl] imide, [BHC]BTA

Experiment and characterisation

Immersion testing

MS specimens: mechanically polished across and along the rolling direction (resultant roughness, Ra, is ~8 nm).

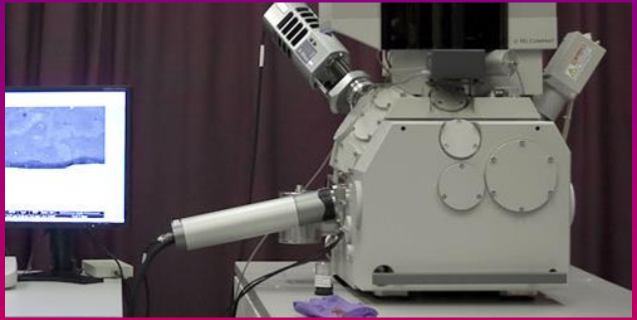
Temperature: room temperature (RT), 60 °C and 80 °C.

Duration: from 1 to 30 days.

Characterisation techniques

SEM/EDX:
Zeiss Ultra-55 scanning electron microscope

XPS:
Kratos Axis Ultra X-ray photoelectron spectrometer



X-ray ultra microscopy, XuM:
Quanta FEG 250 microscope

MnS inclusion-induced corrosion in the ILs with imidazolium-based cations

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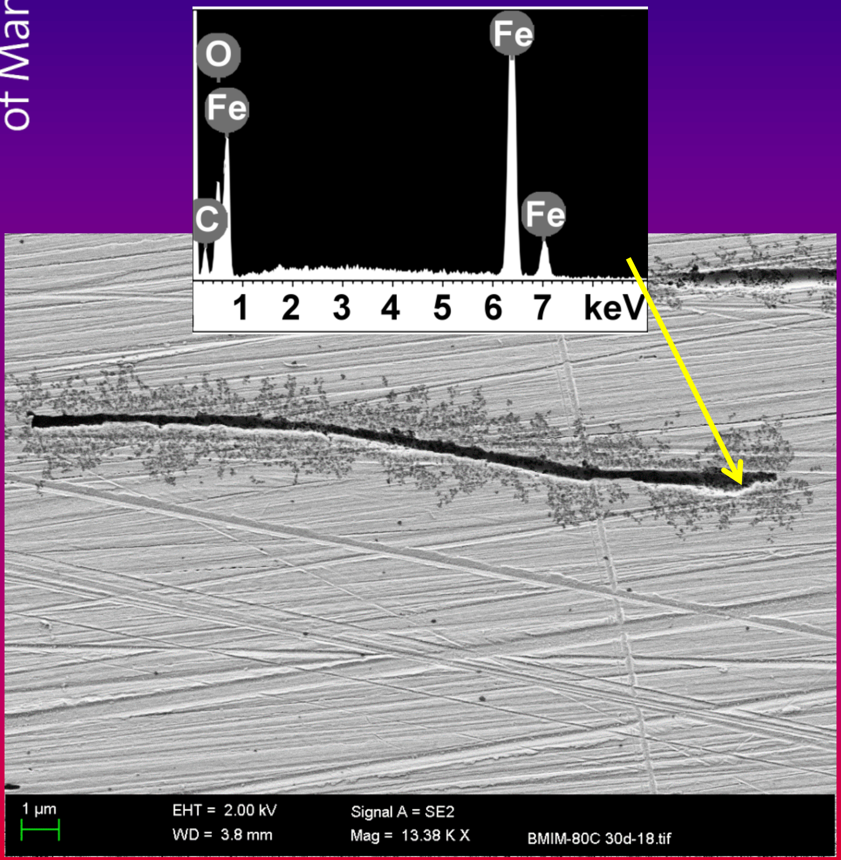
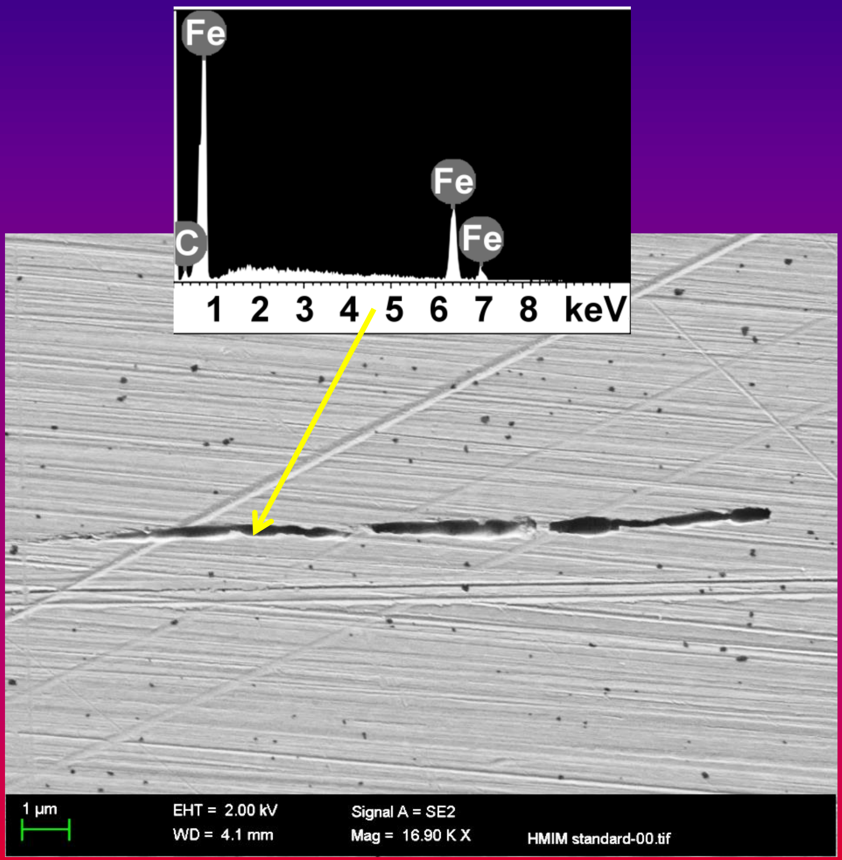
Immersion in [$C_n$mim]TCM

After 30 days of immersion at 80 °C

[C_4mim]TCM



[C_6mim]TCM

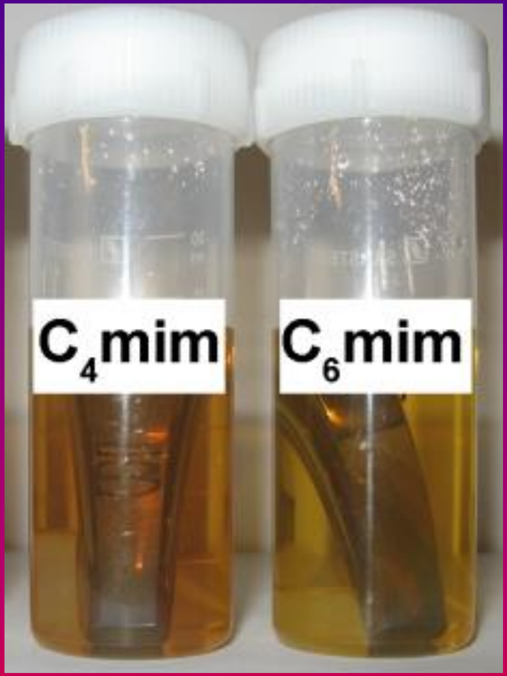


Elongated cavities of various lengths and 200-600 nm width are generated as result of dissolution of MnS inclusions. The oxygen peak in the EDX spectrum after immersion in [C_4mim]TCM is attributed to the presence of corrosion products, e.g. iron oxides. Immersion in [C_6mim]TCM results in dissolution of MnS inclusion without generation of corrosion products (no oxygen peak in the EDX spectrum) that is attributed to the stronger inhibition ability of the IL longer alkyl chain in the cation.

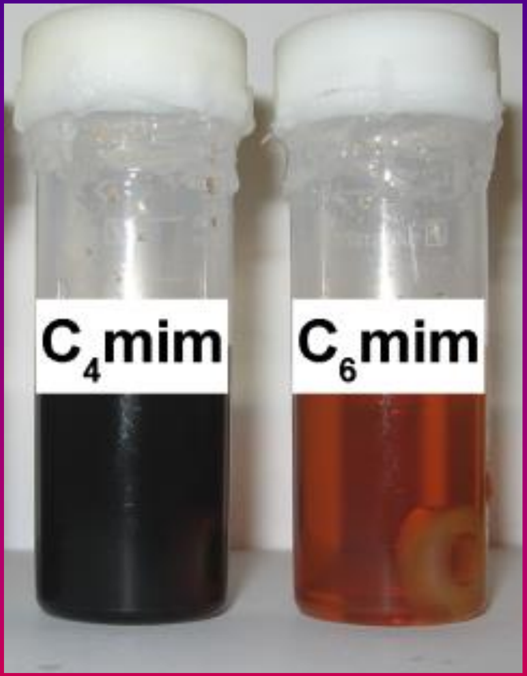
Immersion in [$C_n$mim]TCM

Appearance of the ILs before and after 30 days of immersion of MS at 80 °C

Before immersion



After immersion



Immersion of MS in the [$C_n$mim]TCM ILs results in change of the IL appearance. Higher degree of darkening of [C_4mim]TCM may be attributed to release of iron ions to the IL according to anodic reaction $Fe \rightarrow Fe^{2+} + 2e^-$ at sulphur infected matrix surrounding MnS inclusion sites

Immersion in [$C_n$mim]TCM

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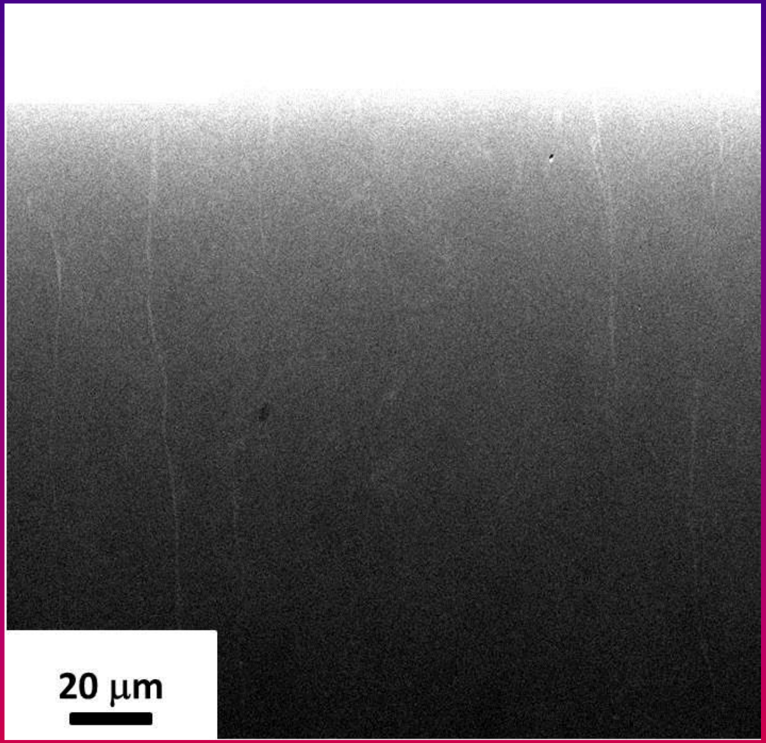
2D X-ray image of the MS plate of 40 μm thickness polished along the rolling direction



Rolling direction

Comparison of the weight (g) of the MS specimens before and after immersion in [C_4mim]TCM and [C_6mim]TCM for 10 and 30 days

	[C_4mim]$^-$	[C_6mim]$^-$
Before	19.98064	20.10528
10 days	19.98041	20.10491
Difference	-0.00023	-0.00037
30 days	19.98041	20.10493
Total difference	-0.00023	-0.00035

Comparison of solubility of MnS in water and IL

	[C_4mim]$^-$	[C_6mim]$^-$
Water content, ppm (KF titration)	2000	1500
Amount of dissolved MnS, μg/ml	11	18
MnS solubility in water present in the IL, μg/ml*	0.0094	0.0071

*Based on the MnS solubility in water of 4.7 μg/ml

The length of individual inclusions may exceed 100 μm.

The weight loss is insignificant after 10-day immersion, suggesting that MnS inclusions are dissolved within 10 days.

The weight loss is mainly attributed to the dissolved MnS inclusions. Its values are more than three orders of magnitude larger than those calculated from the MnS solubility in water that may be attributed to the solubility of inclusions in ILs.

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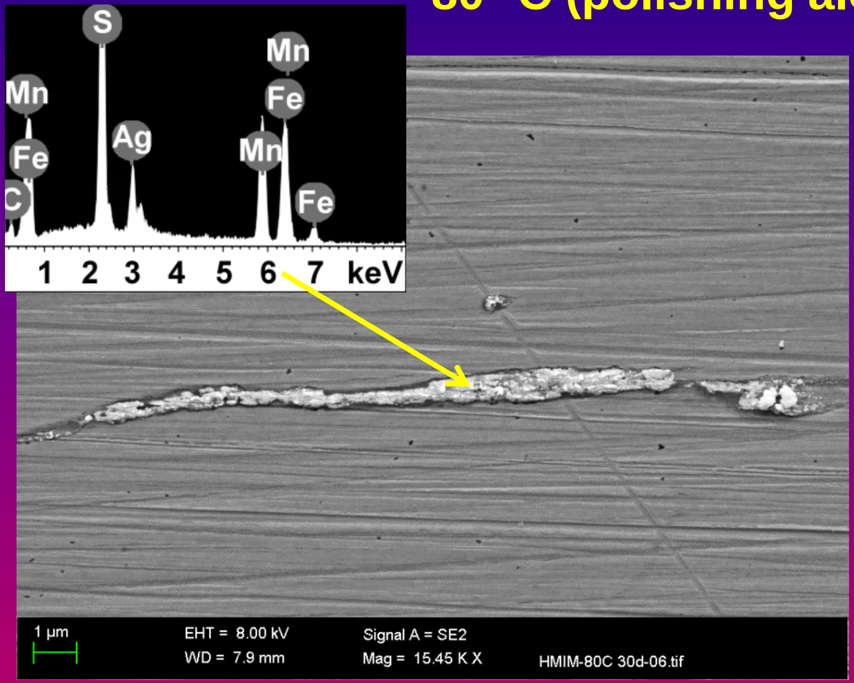
Immersion in [$C_n$mim]TCM

After 30 days of immersion in [C_6mim]TCM contaminated with silver ions at 80 °C (polishing along the rolling direction)



Weight (g) of the MS specimen

Before	19.54027
10 days	19.54037
Difference	-0.00010
30 days	19.54025
Total difference	-0.00002

Silver decoration process

This process is based on reduction of silver ions present in the electrolyte by adsorbed hydrogen atoms:

$H_{ad} \rightarrow H^+ + e^-$,
$Ag^+ + e^- \rightarrow Ag\downarrow$.

Examples of applications:

- hydrogen mapping produced at MnS inclusions in carbon steel or in crevices in iron;
- study the distribution of hydrogen on the surface of platinum, palladium and steel of type 304.

Cathodic reaction at MnS inclusions

$2H^+ + 2e^- \rightarrow H_2$.

Silver ions consume the electrons released in the cathodic reaction and then silver crystals are deposited on the MnS inclusions that prevent their dissolution.

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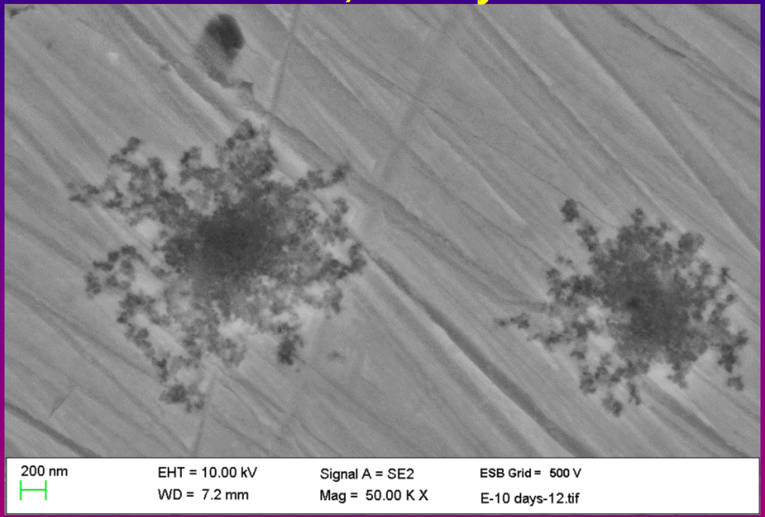
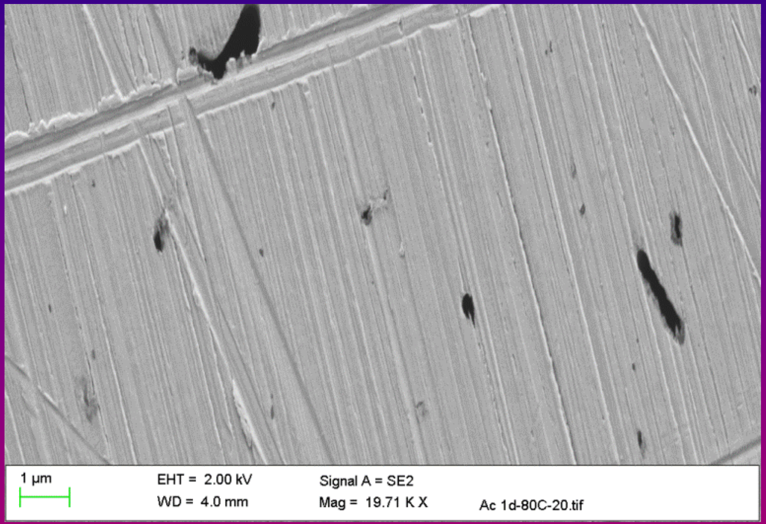
MnS inclusions-induced corrosion: other examples

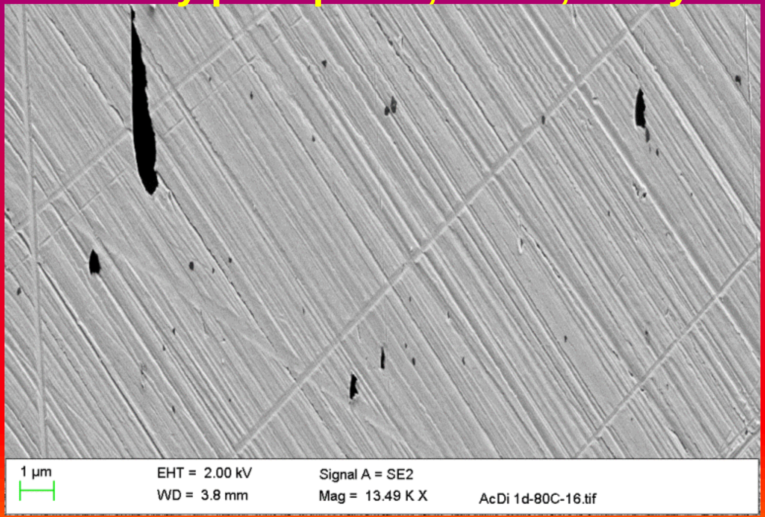
1-ethyl-3-methylimidazolium TCM, 80 °C, 10 days



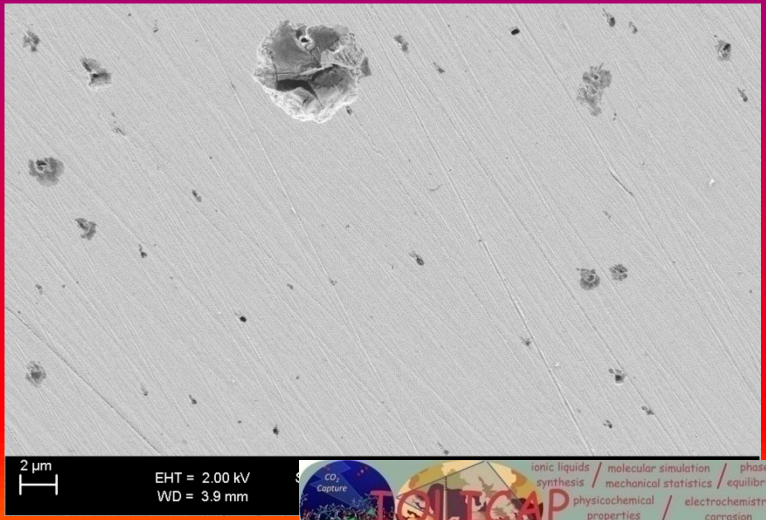
1-ethyl-3-methylimidazolium acetate, 80 °C, 1 day



1-ethyl-3-methylimidazolium diethylphosphate, 80 °C, 1 day



1-[2-(2methoxyethoxy)ethyl-3-methyl-imidazolium TCM, 80 °C, 1 day



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Selective etching in the IL with lactam-based cation

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Immersion in [BHC]BTA

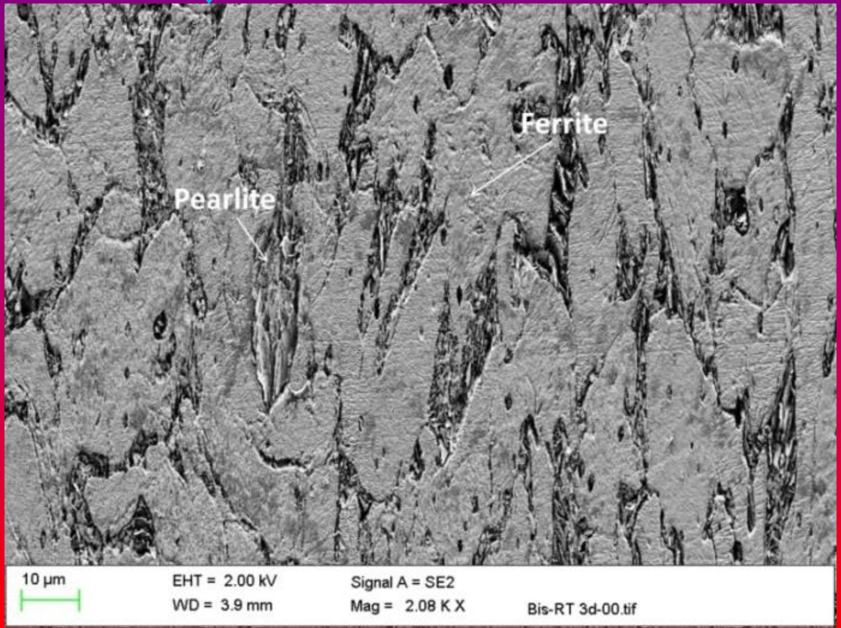
80 ºC, 1 day

80 ºC, 3 days

RT, 3 days

As-polished

RT, 3 days



Comparison of the weights of the specimens of MS before and after immersion in [BHC]BTA*

Immersion conditions	Weight, g		
	Before	After	Difference
1 day, 80 ºC	2.84783	2.76788	-0.07995
3 days, 80 ºC	2.84420	2.64979	-0.19441
3 days, RT	2.46016	2.45928	-0.00088

*the specimens were scrubbed with cotton wool soaked in ethanol to remove corrosion products

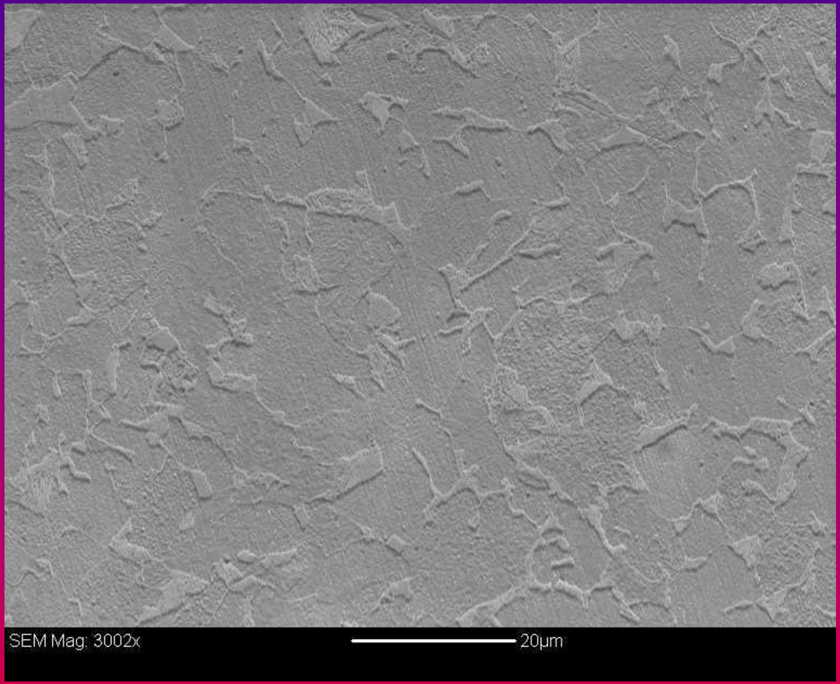
The specimens after immersion in [BHC]BTA are covered by corrosion products. The amount of corrosion products and weight loss increase with temperature and immersion duration.

Interaction with [BHC]BTA results in dissolution of metal over the macroscopic surface, revealing the ferrite regions and pearlite regions with lamellar structure

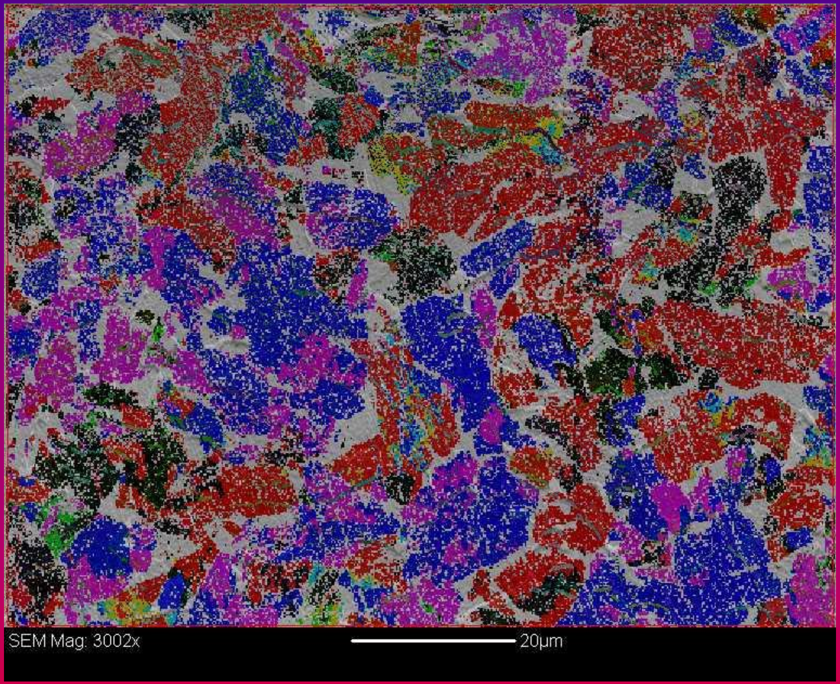
Etching in nital solution

Metallographic examination of MS etched in 2 % nital solution (2 vol. % HNO_3 in ethanol)

Scanning electron micrograph



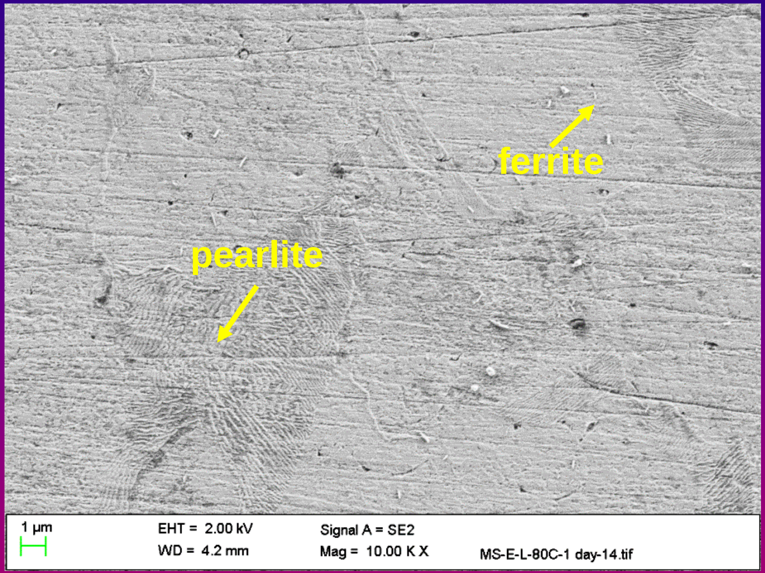
Related EBSD map



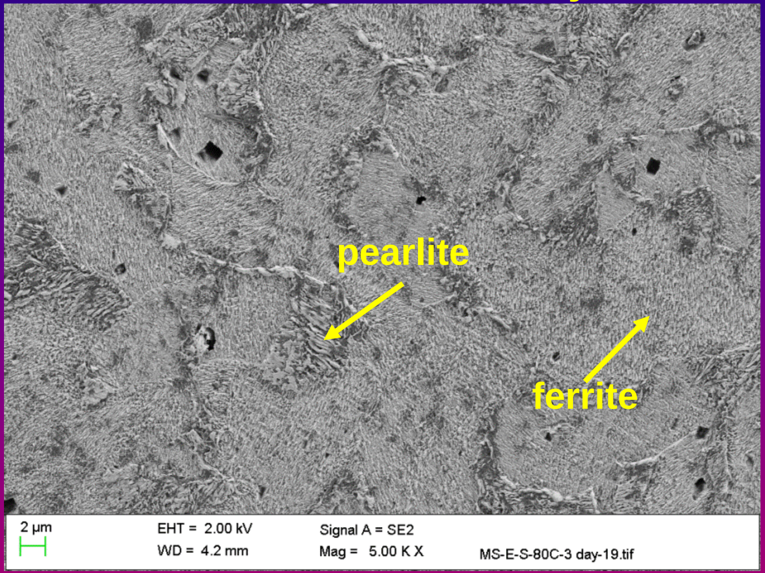
Nital-etched MS reveals pearlite and ferrite regions; in the EBSD map, the pearlite regions of grey appearance are clearly defined.

Selective etching: other examples

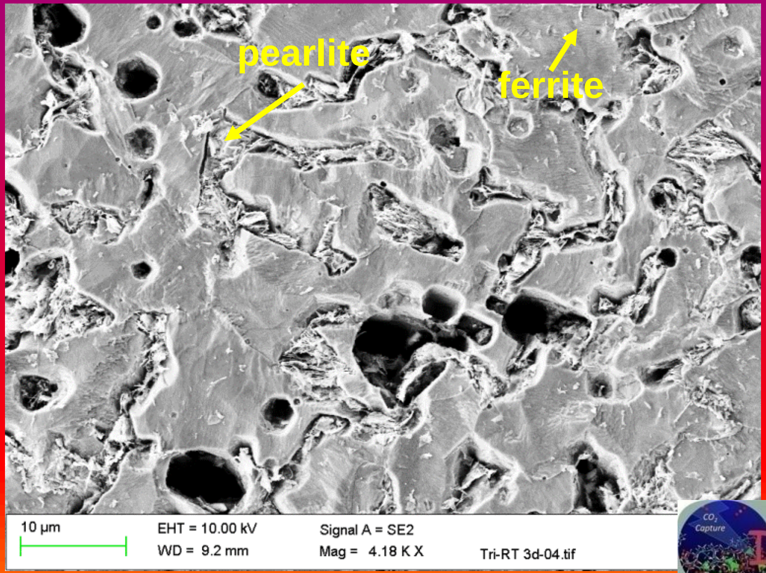
1-ethyl-3-methylimidazolium lysinate, 80 °C, 1 day



1-ethyl-3-methylimidazolium serinate, 80 °C, 1 day



Pyrrolidium-2-one trifluoroacetate, RT, 3 days



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Application of molybdate inhibitor to the IL with lactam-based cation

Immersion in [BHC]BTA with molybdate

IL + 500 ppm MO_4^{2-}, 3 days, RT

IL + 500 ppm MO_4^{2-}, 1 day, 60 °C

Interaction of MS with [BHC]BTA results in dissolution of metal over the macroscopic surface, revealing the pearlite and ferrite phases. The addition of molybdate to the IL reduces significantly the corrosivity of the IL at RT. The inhibition effect also remains strong during immersion at 60 °C for 1 day.

The molybdate is anodic inhibitor and is effective in the presence of oxidising agent such as oxygen. In the presence of oxygen, the releasing divalent ferrous ion is oxidised to trivalent ferric ion that then forms ferric molybdate complex, which is insoluble in basic and neutral solutions:

$$2Fe^{3+} + 3MoO_4^{2-} \rightarrow Fe_2(MoO_4)_3$$

It is speculated that the ferric molybdate layer finally precipitates on the corroding surface thus generating protective film that may additionally contain ferric oxide

Immersion in [BHC]BTA with molybdate

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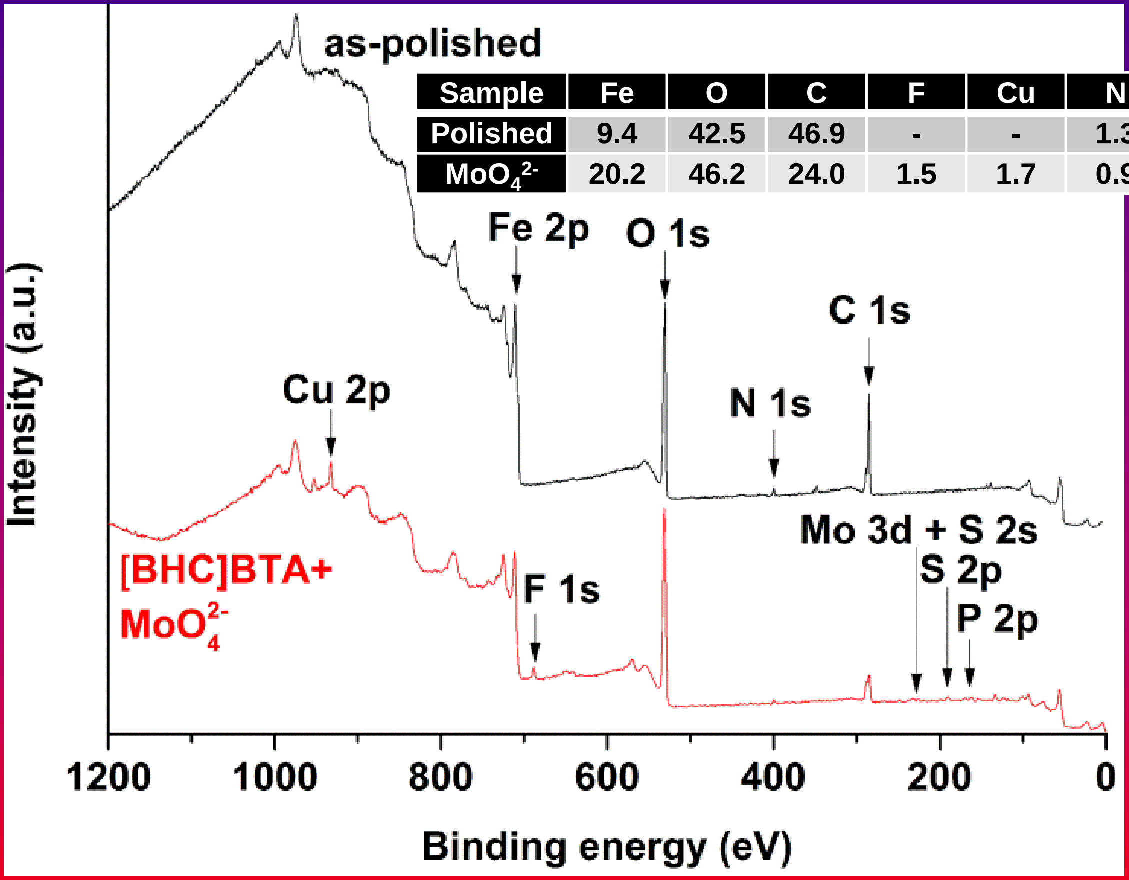
Overview XPS spectra recorded from the MS specimens in the as-polished conditions and after immersion in [BHC]BTA with 500 ppm molybdate at 60 °C for 1 day (the best fits to the experimental data are also displayed)

Sample	Fe	O	C	F	Cu	N	P	S	Mo
Polished	9.4	42.5	46.9	-	-	1.3	-	-	-
MoO_4^{2-}	20.2	46.2	24.0	1.5	1.7	0.9	2.0	1.9	0.3

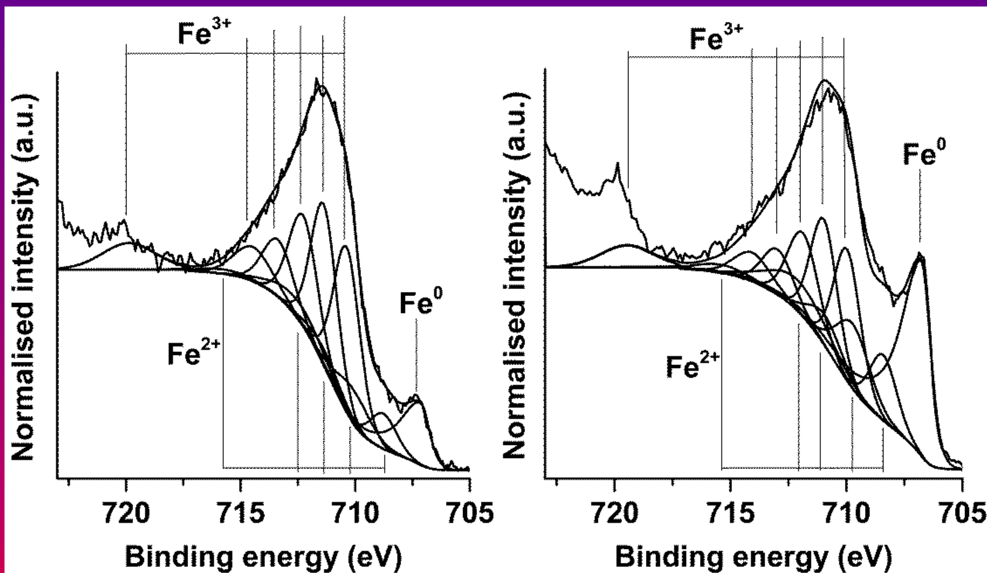


The peaks related to F, C, Cu, P, S and Mo appear in the XPS spectrum of MS after immersion. The F, S, P, Cu and Mo peaks are related to interaction with the IL with added molybdate. The Fe and O peaks are ascribed to iron of MS and oxide film on the surface; C peaks probably originates from surface contamination.

Immersion in [BHC]BTA with molybdate

Higher energy resolution XPS data of the Fe 2p core level

Immersed **As-polished**



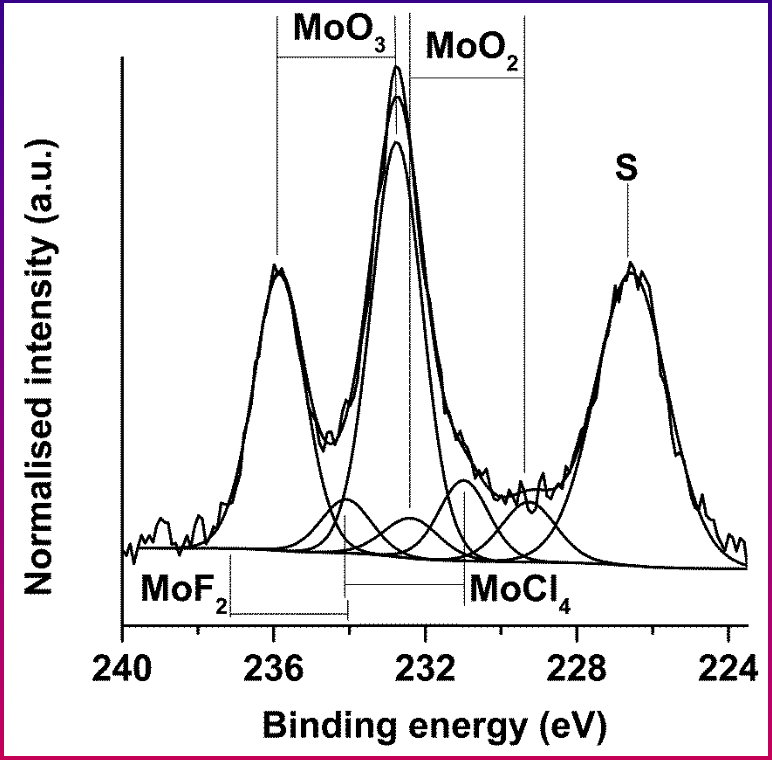
Fe 2p binding energies and relative peak areas after fitting the multiplet split components

Species	As-polished		[BHC]BTA and MoO_4^{2-}	
	Position, eV	Area, %	Position, eV	Area, %
Fe	706.76	25.68	707.15	9.92
Fe^{2+}	708.41	6.44	708.78	4.20
Fe^{2+}	709.71	7.99	710.08	5.21
Fe^{2+}	710.91	3.86	711.28	2.52
Fe^{2+}	712.11	6.81	712.48	4.44
Fe^{2+}	715.41	1.49	715.78	0.97
Total area of Fe^{2+}		26.59		17.34
Fe^{3+}	709.97	12.87	710.37	19.61
Fe^{3+}	710.97	12.25	711.37	18.67
Fe^{3+}	711.87	9.42	712.27	14.35
Fe^{3+}	712.97	5.12	713.37	7.80
Fe^{3+}	714.07	3.87	714.47	5.90
Fe^{3+}	719.47	4.20	719.87	6.41
Total area of Fe^{3+}		47.73		72.74

Multiplet split peaks have been fitted to the Fe 2p region. The iron region Fe 2p reveals the Fe peak centred at 706.8/707.2 eV and a series of components assigned to Fe^{2+} and Fe^{3+} oxides. The increase in the Fe^{3+} component and reduction of Fe component on exposure to molybdate suggest thickening of the oxide film

Immersion in [BHC]BTA with molybdate

Higher energy resolution XPS data of the Mo 3d + S 2p core level of the immersed alloy. The best fits to the experimental data are also displayed.



Optimum Mo 3d + S 2p binding energies

Species	Position, eV
S 2s	226.55
MoO_2 3d5/5	229.27
MoO_2 3d3/2	232.37
MoO_3 3d5/2	232.75
MoO_3 3d3/2	235.85
$MoCl_4$ 3d5/2	230.99
$MoCl_4$ 3d3/2	244.09
MoF_2 3d5/2	234.13
MoF_2 3d3/2	237.23

Two binding energies at 232.75 and 235.85 eV of Mo 3d5/2 and Mo 3d3/2 features imply the presence of hexavalent molybdenum species embedded in the film.

The presence of less intense fit components at binding energies of 229.27 and 232.37 eV corresponding to molybdenum in Mo^{4+} valence state is not clear since in aqueous solutions molybdate is not reduced. However, it was reported elsewhere [M. A. Stranick, Corrosion 40 (1984) 296] on the formation of a non-protective MoO_4 film on the surface of MS in acidic solution containing Na_2MoO_4 due to condensing MoO_4^{2-} ions into various isopolymolybdate anions that further reduce to MoO_2.

The components that may originate from MoF_2 and $MoCl_3$ species may be generated during interaction of molybdate with the IL (fluorine in the anion) or with contamination in the IL (chlorine); however, the statement about formation of fluoride is highly speculative.

Conclusions

Depending on the structure of ionic liquid, the interaction with mild steel results in (i) local changes on the surface at the locations of MnS inclusions and (ii) modification over the macroscopic surface of the alloy.

Long-term inhibiting ability of 1-alkyl-3-methylimidazolium tricyanomethanide ionic liquids ([$C_n$mim]TCM, n = 4 and 6) was confirmed after 30 days of immersion of mild steel at 80 °C. The immersion results in dissolution of MnS inclusions (n = 4, 6) that may be accompanied by formation of corrosion products around the inclusion sites of the ionic liquid with shorter length of alkyl chain in the cation (n = 4).

Accidental addition of silver ions to [C_6mim]TCM resulted in deposition of silver onto the MnS inclusions and prevented inclusions from dissolution.

[BHC]BTA attacks severely the surface of mild steel and results in selective etching of the alloy over the macroscopic surface of the alloy revealing the ferrite and pearlite regions.

Molybdate inhibits etching of mild steel in [BHC]BTA at a concentration of 500 ppm at both room temperature and 60 °C.