

Original citation:

Slater, Carl, Spooner, Stephen, Davis, Claire L. and Sridhar, Seetharaman. (2016) Observation of the reversible stabilisation of liquid phase iron during nitriding. *Materials Letters*, 173 . pp. 98-101

Permanent WRAP URL:

<http://wrap.warwick.ac.uk/80064>

Copyright and reuse:

The Warwick Research Archive Portal (WRAP) makes this work of researchers of the University of Warwick available open access under the following conditions.

This article is made available under the Creative Commons Attribution 4.0 International license (CC BY 4.0) and may be reused according to the conditions of the license. For more details see: <http://creativecommons.org/licenses/by/4.0/>

A note on versions:

The version presented in WRAP is the published version, or, version of record, and may be cited as it appears here.

For more information, please contact the WRAP Team at: wrap@warwick.ac.uk



Observation of the reversible stabilisation of liquid phase iron during nitriding



Carl Slater*, Stephen Spooner, Claire Davis, Seetharaman Sridhar

WMG, University of Warwick, Coventry, UK

ARTICLE INFO

Article history:

Received 2 February 2016

Accepted 8 March 2016

Available online 9 March 2016

Keywords:

Liquid steel

Nitriding

In-situ observation

Phase balance

ABSTRACT

Confocal scanning laser microscopy has been used to observe in-situ cooling of Grade 1 iron whilst under a nitrogen atmosphere. Liquid iron has been stabilised to temperatures below 1400 °C through nitriding at high temperatures. This has been achieved in two ways. Firstly by exposing the melt to nitrogen and observing the onset of solidification whilst cooling. Secondly, under isothermal conditions by re-melting of initially nitrogen free iron at 1400 °C through the introduction of a nitrogen atmosphere. The latter process has been shown to be reversible with liquid iron being unstable once reverting back to a helium atmosphere.

© 2016 The Authors. Published by Elsevier B.V. This is an open access article under the CC BY license (<http://creativecommons.org/licenses/by/4.0/>).

1. Main body

During processing of liquid steel there is tight control of atmospheric conditions. Contact with air is normally avoided by use of protective slag layers, sheathing and inert gas shrouding (usually argon) [1,2]. Both oxygen and nitrogen in the atmosphere can cause major issues later in the processing steps, for example through large/excessive inclusion formation, blow hole formation and embrittlement [3,4]. Due to this less research has been carried out on the potential benefits of adding nitrogen to steel.

After carbon, nitrogen has the next greatest influence on the liquidus temperature (per unit mass) of steel compared to the other more common steel alloying elements [5]. Whilst changing carbon content is a highly controlled method involving solid additions to the liquid steel, nitrogen offers a novel approach for liquidus control due to its gaseous form.

Although much work has been carried out on the benefits of nitriding in the solid state (particularly for stainless steel [6,7]), comparatively little research has been carried out for liquid metallurgy. For example Liapina [8] studied the influence a nitrogen atmosphere has on the stability of iron nitrides. The limited solubility of N in ferrite or austenite results in the formation of stabilizing phases that can tolerate the higher nitrogen content (such as the nitrides γ' and ϵ) [8].

The aim of this work is to look into the stabilisation of liquid iron through ultra-high temperature nitriding. In addition to this the reversible nature of the nitriding process has been studied (due to the implications down stream of high nitrogen contents).

Being able to temporarily change composition at various points during solidification allows for curved/complex paths through the phase diagram on cooling, opening up more novel solutions for problems, as well as the additional benefits of lower melting points for applications such as joining.

For this study Grade 1 pure iron was used ($C < 0.02$, $Mn < 0.2$, $S < 0.015$, $P < 0.015$, all wt%). The samples were machined into small cubes of around 0.2 g. The pseudo-binary Fe-N equilibrium phase diagram can be seen in Fig. 1. The solubility limits of N in iron are well known and governed by Sievert's law [9] and can be seen on the left side of Fig. 1.

A high temperature confocal scanning laser microscope was used in order to observe the in-situ microstructure during solidification of the iron. By focusing light inside a closed chamber onto a point around 1.5 mm diameter, heating rates of > 10 °C/s for the small samples can be achieved. A laser is then used to scan the surface of the sample to give topological information (a more detailed description of this equipment has been given previously [10,11]). The advantage of the enclosed chamber is the ability to control the atmosphere; due to its small size (the sub chamber around the sample is around 100 ml) the chambers atmosphere can be changed in less than two minutes. Before each test the chamber is evacuated to an internal pressure of around 1.3 kPa and ventilated with grade N6 argon gas. The argon passes through three additional oxygen getters to obtain an oxygen concentration below 3 ppm as well as a drying chamber and particle filters. A flow rate of 0.4 L/min at 7 kPa is used (this remains constant for all gases in this study). This process was repeated three times before heating.

Two different thermal profiles were used in this study; the first used continuous cooling from the liquid phase. A calibration

* Corresponding author.

E-mail address: c.d.slater@warwick.ac.uk (C. Slater).

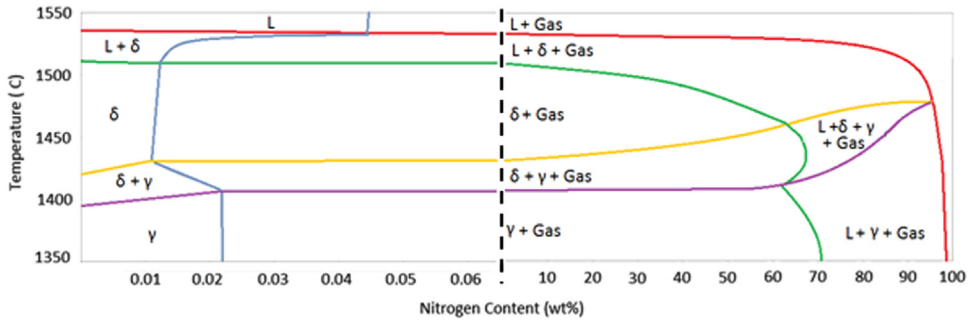


Fig. 1. Phase diagram showing the influence of N on the phase balance in Grade 1 pure iron (which contains low levels of C, Mn, S and P). The left hand side of the diagram shows an expanded section to highlight the equilibrium solubility of nitrogen in the steel.

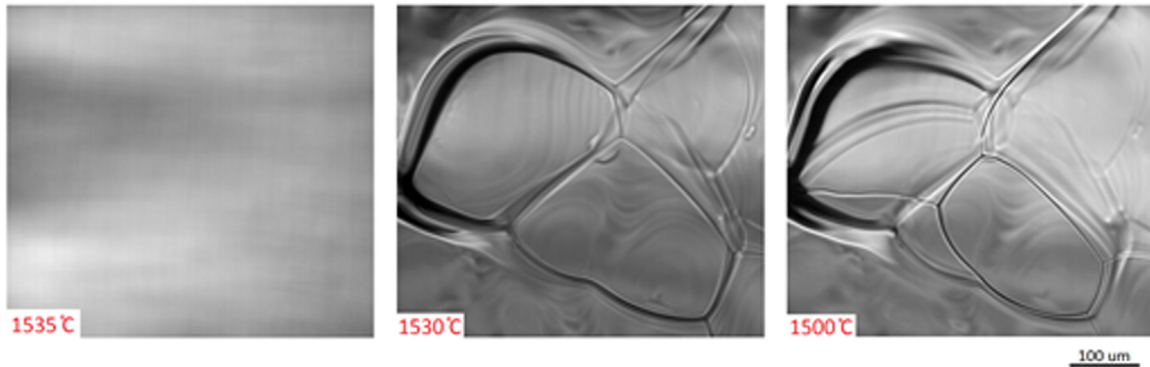


Fig. 2. Time lapse images of Grade 1 pure iron cooled from liquid phase at a rate of 0.5 °C/s in argon.

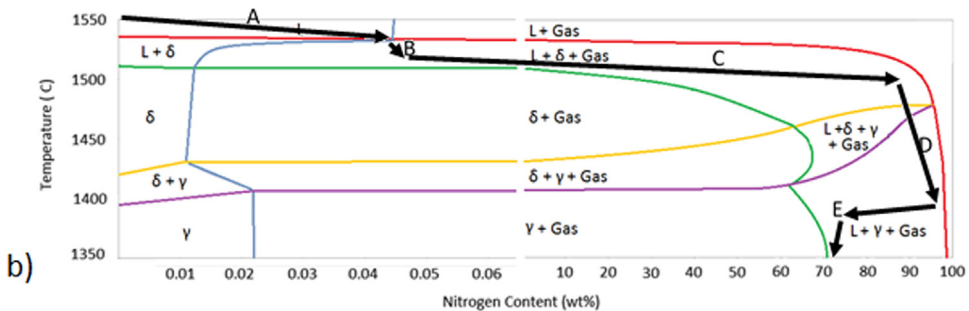
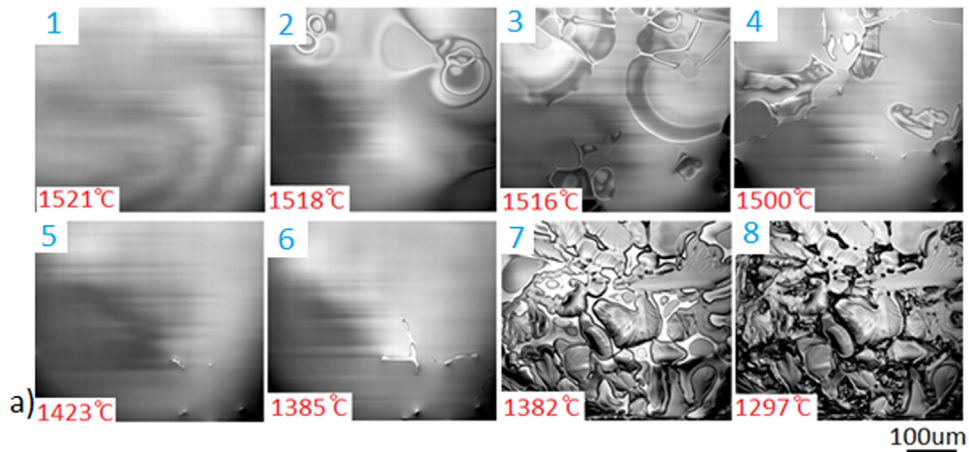


Fig. 3. a) Time lapse images showing liquid iron being cooling in a nitrogen atmosphere b) the composition path taken during cooling.

experiment was carried out for melting and solidification of the Grade 1 pure iron in an argon atmosphere, as argons solubility in liquid steel is minimal (< 1 ppb [12]). The sample was heated at 500 °C/min to 1590 °C to ensure that the sample is completely

molten and held for 1 min, the sample was then cooled at 0.5 °C/s until 1200 °C. A video with recording rate of 10 Hz was used during the cooling period. A series of time lapse images during solidification can be seen in Fig. 2, where the transformation from

liquid to δ -ferrite was observed at around 1532 °C (± 3 °C) with the sample remaining solid thereafter.

The first nitriding experiment was carried out with the sample being initially heated at 500 °C/min to 1590 °C in an argon atmosphere. After holding for 30 s, the atmosphere was switched from argon to nitrogen (grade N5) and the sample was held for a further 30 s (sufficient time to exchange the atmosphere around the sample twice). The sample was then cooled at 0.5 °C/s whilst still under the nitrogen atmosphere and time lapse images can be seen in Fig. 3a.

Fig. 3b shows the phase diagram seen in Fig. 1 overlaid with a schematic representation of the nitrogen content at the surface/in the near surface layer during cooling, which is sub-divided into sections A–E. During the initial hold at 1590 °C (once exposed to a nitrogen atmosphere) and the subsequent cooling to 1520 °C, the liquid iron will start taking up nitrogen to its solubility limit (if exposed for sufficient time to allow equilibrium to be reached). This has been depicted as Section A on the phase diagram and

corresponds to the observation of complete liquid in Fig. 3a.1. It can be seen that solidification initially occurs at a temperature slightly lower (around 1519 °C) than that observed for a sample cooling in argon in Fig. 2.

Further cooling (Section B) takes the sample into the mushy zone, where delta ferrite can be seen to form in Figs. 3a.2-3. However further time results in dissolution of this solid phase (Fig. 3a.4). An explanation for this is that solid iron is known to catalyse the homolytic fission of $N_2 \rightarrow 2N$, and it is in its single atomic form that nitrogen is readily dissolved into the steel. For the nitrogen to be absorbed via this catalytic route, precursor steps of adsorption and fission are required. Adsorption requires a sustained induced dipole through the N_2 molecule; whereas fission is a low energy process and less likely to be rate determining in this instance. The static nature of the solid iron compared to liquid offers a more stable dipole enabling a higher sticking parameter [13]. The geometry of solid iron is also known to offer a low energetic pathway for N_2 dissociation [14]. Both these factors suggest

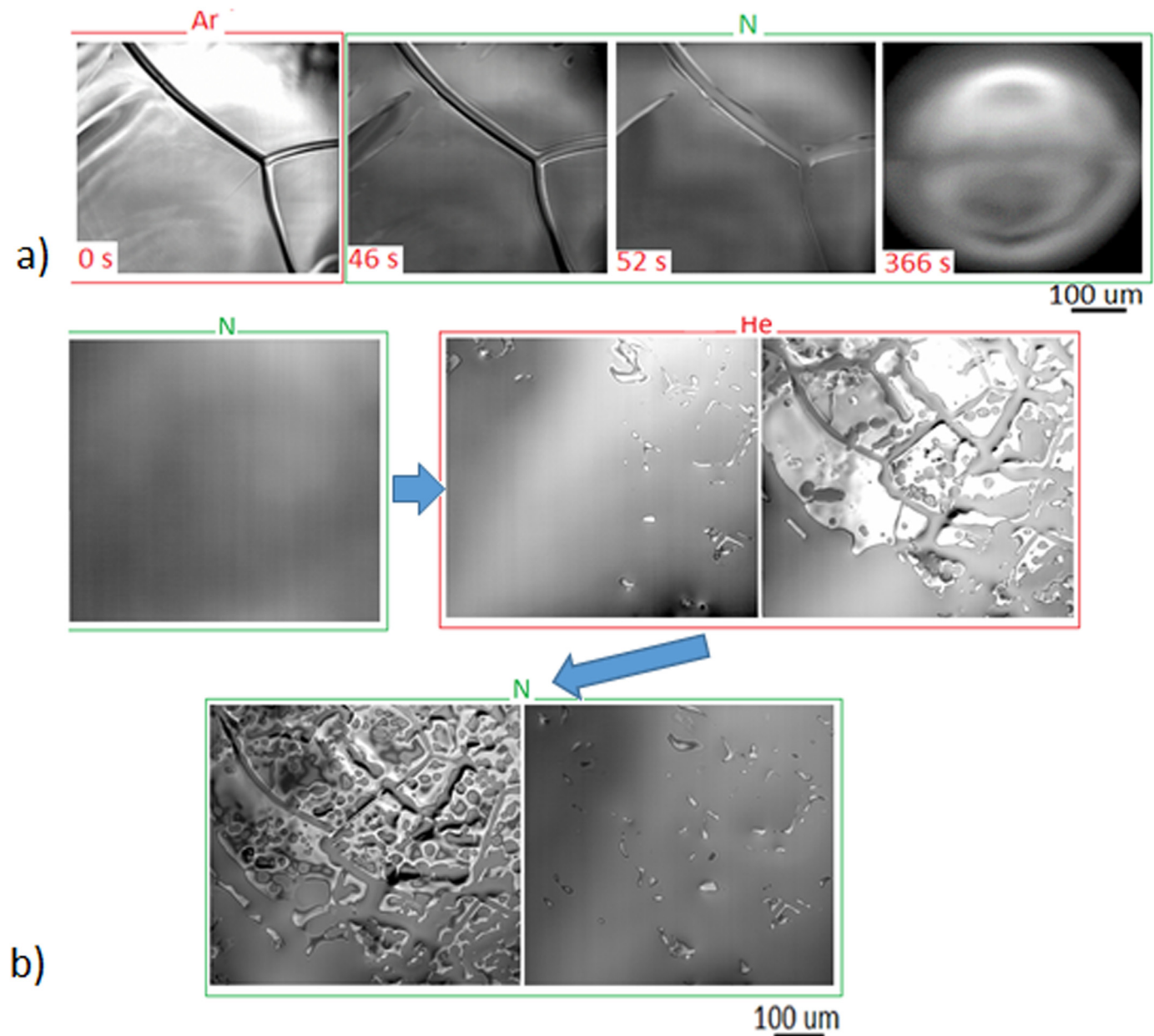


Fig. 4. Time lapse images taken from the isotherm experiments carried out at 1400 °C; a) the time stamp refers to the point the atmosphere was switched to nitrogen and b) shows the stabilisation and destabilisation of the solid phase when the nitrogen atmosphere was removed (replaced by He) and reintroduced respectively.

that solid iron acts as a more efficient catalyst and thus larger amounts of atomic N will be produced, providing the concentration gradient required to form and stabilise higher levels of nitrogen in the iron. This results in the increase in nitrogen content at the surface seen in Section C in Fig. 3b) and the dissolution of solid as it becomes less stable.

A balance then exists between the liquid formed due to the high nitrogen content and the solid fraction needed to maintain the high level of atomic nitrogen. This results in a small fraction of solid remaining during cooling (Fig. 3a.5–6). The liquid – solid phase fraction balance now appears stable during Section D down to 1382 °C where rapid solidification occurs (Section E observed in Fig. 3a.7). At 1380 °C rapid solidification was observed which would suggest a reduction in the nitrogen content at the surface. One possible reason for this is that the solid present (which is cooling as delta ferrite), transforms to austenite (which has a higher solubility for N). This is consistent with the phase diagram allowing for some undercooling to reduce the temperature at which solidification is observed compared to the equilibrium temperature for austenite formation. The solidified material can now tolerate a much higher nitrogen content and therefore diffusion draws nitrogen from the surface further into the sample and from the liquid into the solid, reducing the surface/liquid nitrogen content and further stabilising the austenite at the surface. The subsequent cooling rate did not allow sufficient time for saturation of the austenite as it continues to form and therefore preventing another stabilisation of the liquid phase. The remaining dissolved nitrogen then segregates during solidification, creating small pockets of high nitrogen content, which remain liquid to temperatures below 1300 °C (Fig. 3a.8).

Therefore at the beginning of solidification (fully liquid), the formation of N is the rate limiting step for any significant N dissolution into the iron. However, once some solid iron has formed, the rate of N formation increases dramatically, allowing a much greater concentration of N to develop in the surface, which will also give a more prominent composition gradient into the sample. As a result of the higher nitrogen content, liquid iron is now more stable than delta-ferrite once again. This liquid iron is stable until a much lower temperature (visually observed around 1382 °C), where the driving force for austenite formation becomes too high and it starts to form. The N in the bulk is then concentrated into small pockets that stabilise the liquid for a further 80 °C during cooling. The temperature at which the bulk transformation to solid occurs will depend on the amount of N diffused into the liquid, and therefore dependent on time exposed/cooling rate.

A second test method was used to support this theory. The samples were heated to 1590 °C, held for 1 min and then cooled to 1400 °C in argon (i.e. fully solidified) and held for a further 5 min. After this the atmosphere was switched to nitrogen and the de-stabilisation of the surface was observed. Fig. 4a shows time lapse images from the moment the nitrogen gas was switched on. The process of liquid stabilisation is gradual (taking approximately 5 min), but clearly shows the transformation of the austenite into liquid. This phenomena relies on changes in the N content at the surface of the sample i.e. to increase the N concentration profile through the sample and to force non-equilibrium conditions in the bulk. If N is removed from the atmosphere the concentration gradient (into the iron) is then removed (or even reversed), then the nitrogen is free to diffuse from the bulk to re-establish the

equilibrium state.

This experiment was repeated, however after the 5 min with nitrogen gas flow the atmosphere was switched to helium and the sample was held for another 5 min before switching back to nitrogen once again. This method was used to observe the reversible nature of the nitrogen effect on the liquid iron stability. Fig. 4b shows complete liquid phase at 1400 °C under the nitrogen atmosphere, once helium is introduced, gamma iron once again becomes stable, as the N content reduces, and increases in volume fraction (albeit not to 100% during the time frame observed). The gamma iron then re-melts once the atmosphere is switched back to nitrogen and the N content in the iron increases. This process clearly shows that the level of liquid present at 1400 °C can be controlled simply by changing the atmosphere, although larger scale tests will be needed to quantify the depth to which the N diffuses in iron and the transformation rates.

To summarise, a nitrogen atmosphere has been used to nitride liquid iron with the intent to stabilise the liquid phase to lower temperatures. Using a confocal scanning laser microscope liquid iron has been seen to be stable at temperatures below 1400 °C (a decrease of at least 130 °C compared to a sample solidified in argon). By switching between an inert and nitriding atmosphere the stabilisation of the liquid phase was shown to be at least partially reversible. During continuous cooling in nitrogen, partial solidification occurred at 1515 °C before the majority of the solid transformed back to liquid. It is believed that the solid iron is needed to catalyse the formation of atomic nitrogen which then stabilises the liquid phase at the lower temperatures. With surface melting shown to be possible and stable to the lowest temperatures reported, field processes such as powder sintering, crack repair and joining may greatly benefit from this phenomenon.

Acknowledgement

The authors would like to thank EPSRC for funding (Grant number EP/M014002/1) and also WMG for their support and facilities.

References

- [1] S. Louhenkilpi, in: S. Seetharaman (Ed.), *Treatise Process Metallurgy*, Elsevier, Boston, 2014, pp. 373–434.
- [2] P. Hayes, E. Jak, *Treatise on Process Metallurgy*, Elsevier, United States, 2014.
- [3] F.W. Scott, *Ind. Eng. Chem.* 23 (1931) 1036–1051.
- [4] E.T. Turkdogan, *Fundamentals of Steelmaking*, Maney Publishing for IOM3, the Institute of Materials, Minerals and Mining, United Kingdom, 1996.
- [5] Thermo-Calc Software TCFE7 Steels/Fe-alloys database version 7.
- [6] B.C.E.S. Kurelo, G.B. de Souza, S.L.R. da Silva, F.C. Serbena, C.E. Foerster, C. Alves, *Appl. Surf. Sci.* 349 (2015) 403–414.
- [7] Y. Li, S. Zhang, Y. He, L. Zhang, L. Wang, *Mater. Des.* 64 (2014) 527–534.
- [8] T. Liapina, *Univ. Stuttgart*, 2005.
- [9] C.L. Briant, *Impurities in Engineering Materials - Impact Reliability and Control*, Taylor & Francis, United Kingdom, 1999.
- [10] D. Phelan, M. Reid, R. Dippenaar, *Comput. Mater. Sci.* 34 (2005) 282–289.
- [11] A.N. Assis, J. Warnett, S. Spooner, R.J. Fruehan, M.A. Williams, S. Sridhar, *Metal. Mater. Trans. B* 46 (2014) 568–576.
- [12] R. Boom, A.A. Kamperman, O. Dankert, A. Veen, *Metal. Mater. Trans. B*, vol. 31, n.d., pp. 913–919.
- [13] G. Ertl, S.B. Lee, M. Weiss, *Surf. Sci.* 114 (1982) 515–526.
- [14] I. Goikoetxea, M. Alducin, R. Diez Muino, J.I. Juaristi, *Phys. Chem. Chem. Phys.* 17 (2015) 19432–19445.