P.J. Mohlala and C.A. Strydom,
S. Afr. J. Chem., 2007, **60**, 29–35,
<http://journals.sabinet.co.za/sajchem/>.

Lewis Acid-Base Properties of a Low Carbon Aluminium Killed Steel Substrate

Pheladi J. Mohlala[a] **and Christien A. Strydom**[b]*

[a]*Industrial Metals and Minerals Research Institute (IMMRI), University of Pretoria, Pretoria, 0002 South Africa.*
[b]*School of Chemistry, North-West University, Potchefstroom Campus, Potchefstroom, 2520 South Africa.*

Received 12 January 2007; revised 26 March 2007; accepted 2 May 2007.

ABSTRACT

An important factor in achieving maximum adhesion of a particular coating system to the substrate lies in the proper preparation of the substrate prior to the application of paint. The Lewis acid-base properties of the outer metal surface play a determinant role in many of these applications, and the chemical reactions involved therein. In this work, the wetting properties of a low carbon aluminium killed (LCAK) substrate have been largely modified by a chemically activated surface treatment. XPS analysis was performed on the surface. Wettability in water, a polar and protic probe liquid, and in α-bromonaphthalene, a non-polar and aprotic probe liquid, of the LCAK surface is strongly modified when the LCAK surface is treated with dilute formic acid and warm water. Formic acid forms formate ions which have a higher reactivity with respect to molecular species and are able to react with the exposed surfaces, changing the relative structure of the hydroxyl layer.

KEYWORDS

XPS, Lewis acid-base, wettability, steel, surface.

1. Introduction

The adhesion of paint to a substrate is affected by the nature and conditions of the substrate and by the nature and composition of the paint. The study of acid-base properties of coatings and substrate surfaces is of fundamental significance in adhesion. Many methods have been proposed in the literature to understand and quantify the acid-base interactions at the interfaces.[1] Fowkes proposed describing adhesion in terms of acid-base or electron donor-acceptor interactions.[2,3] Fowkes then considered non-dispersive interactions to be identical to electron donor-acceptor or Lewis acid-base interactions. (A Lewis acid is any substance that can act as an electron-pair acceptor and a Lewis base any substance that can act as an electron-pair donor).

Polar molecules used to determine the specific interactions with the solid substrate are characterized by their donor (DN) and acceptor (AN) numbers.[4] The concept of donor-acceptor interactions is an extension of the Lewis acid-base theory, dealing with coordinate bonds, which are formed by sharing a pair of electrons between donor and acceptor species.

The characterization and quantitative description of forces at the interface constitute an important study area in interface science.[5,6] Its solution would allow the analytical prediction and explanation of material behaviour at interfaces through the quantification of the interactions and, as an immediate outcome, the capability to design polymeric coatings for a specific purpose.

Often particular steel is chosen as a substrate for coatings because it has given satisfactory performance in similar applications elsewhere, but as the limits of its properties are approached other grades have to be considered. A comprehensive knowledge of the range and variety of steels, together with their uses, is required in order to select steel which will give satisfactory performance. Much written information is available on steels but considerable experience is required in order to select steel for a particular use.[7–9] Low carbon aluminium killed (LCAK) steel (steel deoxidized with aluminium in order to reduce the oxygen content to a minimum so that no reaction occurs between carbon and oxygen during solidification) was considered. This type of steel is used mostly by the packaging industry. Organic coatings are used not only for decorative purposes but also for labelling the content of LCAK steel containers. The surface condition of the steel used for low-cost, mass-produced items is more critical, where extensive surface preparation is typically done prior to the application of organic coatings.

1.1. Surface Tension and Contact Angle Theory

1.1.1. *Surface Tension Components (STC)*

Surface tension is a measure of the cohesive energy present at the interface. Fowkes[2] originally proposed the surface tension of a system to consist of the components:

$$\gamma = \gamma^{\mathrm{d}} + \gamma^{\mathrm{i}} + \gamma^{\mathrm{p}} + \gamma^{\mathrm{h}}, \qquad [1]$$

where the superscripts d, i, p and h represent dispersion, induction, polarization and hydrogen bonding. Later Fowkes[10] defined the acid-base component, γ^{AB}, to include the last three terms on the right hand side of Eq. [1] as follows:

$$\gamma^{\mathrm{AB}} = \gamma^{\mathrm{i}} + \gamma^{\mathrm{p}} + \gamma^{\mathrm{h}}. \qquad [2]$$

However, according to Fowkes and van Oss, Chaudhury and Good (VCG),[11] both the induction (i) and polarization (p) components are of secondary importance in comparison with the dispersion (d) and hydrogen bonding (h) components, so VCG suggested that the first three components on the right hand side of Eq. [1] should be combined into the Lifshitz-van der Waals components, γ^{LW}, instead:

$$\gamma^{\mathrm{LW}} = \gamma^{\mathrm{d}} + \gamma^{\mathrm{i}} + \gamma^{\mathrm{p}}. \qquad [3]$$

Then, the acid-base component of surface tension represents only hydrogen bonding.

$$\gamma^{\mathrm{AB}} = \gamma^{\mathrm{h}}. \qquad [4]$$

---

* To whom correspondence should be addressed. E-mail: christien.strydom@nwu.ac.za

The total surface tension for a 'polar' system then becomes:

$$\gamma = \gamma^{\mathrm{LW}} + \gamma^{\mathrm{AB}} \,. \qquad [5]$$

VCG further divided the asymmetric hydrogen-bond part of the dipolar system into two separate factors: a hydrogen-bonding acidic parameter, γ^{+}, which is identical to the contribution of the proton donor, and a hydrogen-bonding basic parameter, γ^{-}, associated with the proton acceptor.

1.1.2. *Contact Angle Components*

In the case of contact angle measurements, surface energy is determined by wetting the surfaces of solids with different liquids. Young's equation allows a calculation of the stationary wetting angle under certain conditions. It describes the equilibrium of forces between the surface tension terms at a three-phase boundary. When a liquid droplet is placed on a homogeneous smooth solid surface, the contact angle, θ, can be obtained using Young's equation:[12]

$$\cos\theta = \frac{\gamma_{\mathrm{sv}} - \gamma_{\mathrm{sl}}}{\gamma_{\mathrm{lv}}} \,, \qquad [6]$$

where γ_{sv}, γ_{sl}, and γ_{lv} are the surface/interfacial tensions of the solid-vapour, solid-liquid and liquid-vapour phases, respectively.

Now the total surface tension is the sum of polar and non-polar components:

$$\gamma_i = \gamma_i^{\mathrm{LW}} + \gamma_i^{\mathrm{AB}} \,. \qquad [7]$$

However, whilst γ_i^{LW} suffices for the description of the non-polar part of the surface tension of *i*, γ_i^{AB} is composed of *two different surface tension parameters,* namely the parameter representing its electron-accepticity, designated as γ_i^{+}, and the parameter representing its electron-donicity, designated as γ_i^{-}, such that

$$\gamma_i^{\mathrm{AB}} = 2\sqrt{\gamma_i^{+}\gamma_i^{-}} \,. \qquad [8]$$

The total acid-base Gibbs energy of interaction between two polar materials (i and j) may be expressed as:[12]

$$\Delta G_{ij}^{\mathrm{AB}} = -2\left(\sqrt{\gamma_i^{+}\gamma_j^{-}} + \sqrt{\gamma_i^{-}\gamma_j^{+}}\right). \qquad [9]$$

Using the Young-Dupré equation:[13]

$$(1+\cos\theta)\gamma_i = -\Delta G_{ij} \,, \qquad [10]$$

Equation [7] can be re-expressed as:

$$\Delta G_{ij}^{\mathrm{TOT}} = \Delta G_{ij}^{\mathrm{LW}} + \Delta G_{ij}^{\mathrm{AB}} \,, \qquad [11]$$

where ΔG^{LW}, the Lifshitz-van der Waals interaction, is a non-covalent interaction that involves permanent dipoles within the molecules, and ΔG^{AB}, the Lewis acid-base interaction is a hydrogen bonding interaction between electron-donor and acceptor.

Therefore the Young-Dupré equation [10] can be re-expressed as:

$$(1+\cos\theta)\gamma_i = 2\left[\sqrt{\gamma_i^{\mathrm{LW}}\gamma_j^{\mathrm{LW}}} + \sqrt{\gamma_i^{+}\gamma_j^{-}} + \sqrt{\gamma_i^{-}\gamma_j^{+}}\right] \,. \qquad [12]$$

In the above expressions of the Young equation, *i* represents the liquid and *j* the solid. The Young-Dupré equation relates the contact angle to the surface and interfacial tensions.[12]

So far several theories on solid surface Gibbs energy determination and approaches have been proposed, but formulation of surface and interfacial Gibbs energy is still a very debatable issue. Chibowski and Perea-Carpio[14] addressed the problems of contact angle and solid surface Gibbs energy determination. In their study they clearly showed that direct calculation of the contact angle from Washburn's equation, which was then applied in Young's equation, led to erroneous results of the solid surface Gibbs energy components. However, Costanzo, Giese and van Oss[15] determined the acid-base characterization of clay mineral surfaces by contact angle. They showed that contact angle determination can be done for swelling clay minerals as well as for non-swelling clay minerals. Pinzari and his co-workers[16] have studied surface acid-base properties of titanium and an oxidized titanium sheet. Both from their wettability and adsorption studies they found a basic behaviour for the titanium metal and acidic behaviour for the oxidized titanium metal.

Table 1 Composition details of low carbon aluminium killed steel.

Steel	C	Mn	S	Si	Cu	Ni	Cr	Al
LCAK	0.047	0.2	0.003	0.018	0.008	0.006	0.025	0.059

In this work, the wetting properties of LCAK substrate have been largely modified by a chemically-activated surface treatment. The surface was investigated through XPS analysis and contact angle measurements. Wettability in water, a polar and protic probe liquid, and α-bromonaphthalene, a non-polar and aprotic probe liquid, of LCAK surfaces may be strongly modified when the LCAK surface is treated with dilute formic acid and warm water. In this way formic acid produces formate ions which have a higher reactivity[17] and are able to react with exposed surfaces, changing the relative structure of the hydroxyl layer.

2. Experimental

2.1. Standard Surface

Low carbon aluminium killed steel (LCAK) was used; the composition of the steel is given in Table 1. All samples were mounted and polished to a 5 μm finish. The standard sample was washed in hebitex (inhibited hydrochloric acid with organic additives that tend to coat the cleaned steel to inhibit the attack on the steel) to remove any existing oxide layer, rinsed in tap water at room temperature to prevent the possibility of organic contamination on the surface, which could influence the wettability, and then cleaned with Radchem 99.9% absolute ethanol (A.R.) to remove the water film, followed by a hot air drying step to prevent the formation of corrosion on the surface.

2.2. Test Liquids

The test liquids were carefully chosen to cover a range of surface tensions and viscosities (Table 2). Surface tension measurements were performed on a Ramé-Hart imaging system. The liquids were injected with a syringe to form a drop on the tip of the needle. The drop was observed optically and the surface tension was calculated from the shape of the drop using the Young-Laplace equation. In this experiment, the surface tension of the liquid solution was determined against air using the pendant drop shape method.

2.3. Contact Angle

The procedure used to measure the contact angle is based on the ASTM D724 standard. The image of each single drop was acquired by a video-camera connected to a computer. The value of the contact angle, θ, was calculated by measuring the base (*b*) and height (*h*) of the drop profile and using the relationship:[18]

$$\theta = \arcsin\left(\frac{4bh}{4h^2 + b^2}\right). \qquad [13]$$

The following surface treatments were performed prior to the contact angle measurements.

Table 2 Test liquids and their properties at 25 °C.

Liquids	Density/ g cm^{-3}	Viscosity at 25 °C/ cp	Surface tension/ mN m^{-1}	Contact angle of the reference sample/°
Water	0.997	0.89	72.2	31.2
Hexane	0.659	0.510	18.5	3.5
Xylene	0.860	0.620	24.4	6.3
α-Bromonaphthalene	1.48	1.65853	40.5	11.1

2.3.1. *Warm Water Treatment*

The polished sample was rinsed in warm water at *ca.* 40 °C which was previously boiled for four hours to remove oxygen, and then cleaned with ethanol to remove the water film, followed by a hot air drying step to prevent the formation of corrosion on the surface.[19]

2.3.2. *Formic Acid Treatment*

The sample was rinsed in 1:1 v/v Saarchem 85% chemically pure formic acid (A.R.) and then cleaned with ethanol to remove the water film, followed by a hot air drying step.

2.3.3. *Non-Formic Acid Treatment*

After polishing, the sample was rinsed in ethanol, followed by a hot air drying step.

Surface treatment was performed for 10 min. Exposure of the LCAK surface to the laboratory ambient was minimized by performing the contact angle measurements of water and α-bromonaphthalene immediately after surface treatment. This reduces the effects on the measurements of slow buildup of an adsorbed organic layer. The contact angle measurements of all treated (LCAK) surfaces were measured in the laboratory ambient using a Ramé-Hart Inc. goniometer imaging system.[20] A drop of a fixed volume ($\sim$2 μL) was formed on the end of a syringe needle and lowered into contact with the surface. As the needle was raised, the drop detached from the tip and advanced across the surface. The sessile drop was observed optically and the contact angle was calculated from the shape of the drop using Young's equation. Contact angle measurements were performed with deionized water and Fluka 95.0% α-bromonaphthalene (GC) at room temperature. The contact angles were measured within 30 s of detachment.

2.4. XPS Analysis

To obtain chemical information on induced surface modifications and on their influence on wettability behaviour, X-ray photoelectron spectroscopy (XPS) analysis was carried out on the reference sample (sample without surface modification), formic acid treated sample, non-formic acid sample and sample treated with warm water.

The XPS spectra were obtained using a PHI spectrometer (model 5400) equipped with Mg/Al dual mode source and a small area analyser with PSD detector. An achromatic Mg K_α X-ray (1253.6 eV) source was operated at 300 W. The vacuum pressure was 10^{-8} Torr during spectra acquisition. Survey spectra were obtained at a take-off angle of 45 °. The C 1s and O 1s regions were recorded.

2.5. Wettability

The term 'wetting', in general, is connected with the area covered by a liquid drop placed on a solid surface. It varies on the basis of the liquid and surface and it is measured by the contact angle, defined as the angle between the drop and the surface, as shown in Fig. 1.[21] When the contact angle has a value near zero, the liquid is said to wet the surface perfectly, otherwise it is said not to wet the surface.[22] The procedure to measure the contact angle is described in the ASTM D724 standard.[18]

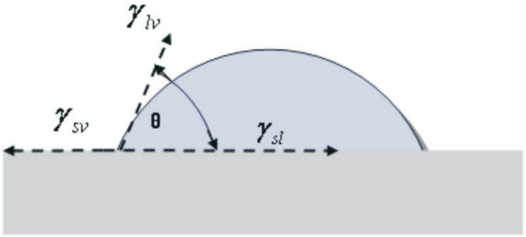

Figure 1 Contact angle and gas–liquid–solid related tensions.

Table 3 The pH values of the acidic and basic solutions.

	Concentration/ mol L^{-1}	pH
Acidic	1	0.8
	2.0×10^{-2}	2.5
	4.0×10^{-4}	3.6
	3.0×10^{-6}	4.1
Basic	1	13.1
	1.0×10^{-2}	12.1
	2.0×10^{-5}	10.5
	4.0×10^{-6}	9.1

Hydrochloric acid (32%) (A.R.) and sodium hydroxide pellets (A.R.) from Promark Chemicals were used. Un-buffered aqueous solutions representing both acid and basic conditions were prepared. The concentrations of the acidic solutions were approximately 1.0 mol L^{-1}, 2.0×10^{-2} mol L^{-1}, 4.0×10^{-4} mol L^{-1} and 3.0×10^{-6} mol L^{-1}, while the concentrations of the basic solutions were approximately 1.0 mol L^{-1}, 1.0×10^{-2} mol L^{-1}, 2.0×10^{-5} mol L^{-1} and 4.0×10^{-6} mol L^{-1}. The pH was measured using a Labotec Orion 410A+ basic pH meter with an Orion 91-65 Ag/AgCl electrode in the temperature range 0 to 100 °C, calibrated with solutions of pH 4 and 10. The pH values of the acidic and basic solutions are shown in Table 3. The influence of pH on the wettability (contact angle) of a standard polished sample of LCAK and a warm water treated sample of LCAK was determined. The wettability measurements on the samples were performed making use of the liquids prepared as in Table 3. The primary effect here is the acid-base interaction of the solutions and the surface. Other factors such as ionic strength influences were neglected.

3. Results and Discussion

Most metal surfaces are composed of metal oxide. In the laboratory ambient, the oxides at the surface hydrate to form a high density[23,24] of hydroxyl groups (1 to 5 hydroxyl groups per 10^{-8} m^2 of surface area). Practically, such a surface can be represented as $MO_m(OH)_n$, where M is a metal. The surface hydroxyl groups adsorb water molecules via hydrogen bond interactions,

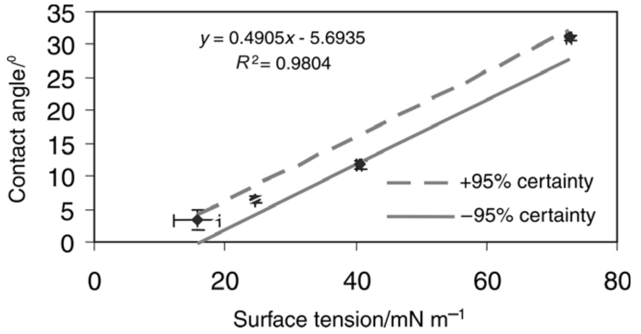

Figure 2 The relationship between contact angle and surface tension.

wherein the surface acts as either the acid or the base. An acidic surface site shows a tendency to donate a proton or a cation or to accept electrons or an anion, whereas a basic surface site shows a tendency to accept a proton or a cation or to donate electrons.[25]

3.1. Surface Tension and Contact Angle

As demonstrated in Fig. 2, low surface tension systems were found to yield low contact angles. The liquids were not of the same family and thus had diverse properties (Table 2). The contact angle increases with increasing surface tension, indicating that for a given surface, better wetting is obtained for the lower surface tension liquids. Water contact angles were determined to ensure surface cleanliness on the polished LCAK substrates prior to treatment, and it was found that a drop of water produced an average contact angle of approximately 31.2 ° in this case. For hexane, xylene and α-bromonaphthalene, contact angles of 3.5 °, 6.3 ° and 11.1 ° were measured, respectively.

3.2. Contact Angle of Treated Surfaces

The contact angle results for the treated surfaces are summarized in Table 4. LCAK surfaces activated chemically with warm water strongly enhance wettability behaviour when compared with other surface treatments. This is suggested by the spreading of the water and of the α-bromonaphthalene on the warm water treated surface, where contact angles of 28.8 ° and 4.9 °, respectively, were observed.

Table 4 Contact angles of liquids on a standard LCAK sheet.

Sample	Surface treatment	Liquid	Contact angle/°
1	formic acid	water	42.5
2	formic acid	α-bromonaphthalene	9.5
3	non-formic acid	water	45.2
4	non-formic acid	α-bromonaphthalene	13.4
5	warm water	water	28.8
6	warm water	α-bromonaphthalene	4.9

3.3. XPS Analysis

In Fig. 3 the XPS survey spectrum obtained for the reference low carbon aluminium killed (LCAK) sheet is shown. Carbon contamination is clear from Fig. 4. The main carbon peak (I) at 285.2 eV is attributed to hydrocarbon C (C-H) and peak (II) at 289.1 eV to carbonates (C=O).[16] The O 1s peak (Fig. 5) shows three components that were attributed to adsorbed water (H_2O), hydroxyl (OH) and oxides (OOH).[19] The XPS peak maxima of the O 1s species for the other samples are shown in Table 5.

An estimated correlation (Table 6) is determined between the $Fe(OH)_2$ and Fe(OOH) peak heights. Peak heights or areas are directly related to the concentrations of the species on the surface. From previous work, good paint adhesion of Lewis-base alkyd paint was associated with a 1:1 ratio of $Fe(OH)_2$ and Fe(OOH) species on the surface of the steel.[26]

The Lewis acid-base properties of a hydroxyl group depend on the electronegativity values of the species to which it is bonded.[16] For $Fe(OH)_2$, the hydroxyl groups are bonded to Fe^{2+}, which make them Lewis base species and for Fe(OOH) the hydroxyl groups are bonded to oxides and are thus Lewis acid species.[26]

3.4. Wettability

In Figs 6 and 7, the acid-base contact angle curves of the reference and warm water treated LCAK sheet are shown respectively. The samples show changes in the contact angle as a function of the pH with opposite behaviour.

Fe(OOH) and $Fe(OH)_2$ were characterized and distinguished

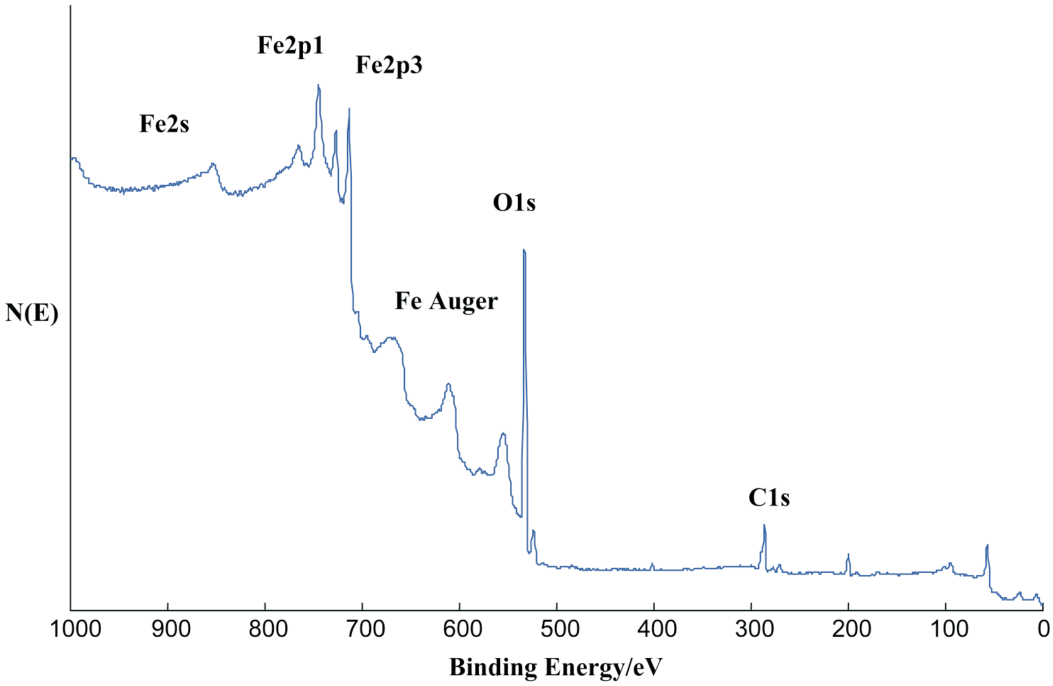

Figure 3 XPS survey spectrum obtained for the reference low carbon aluminium killed (LCAK) steel.

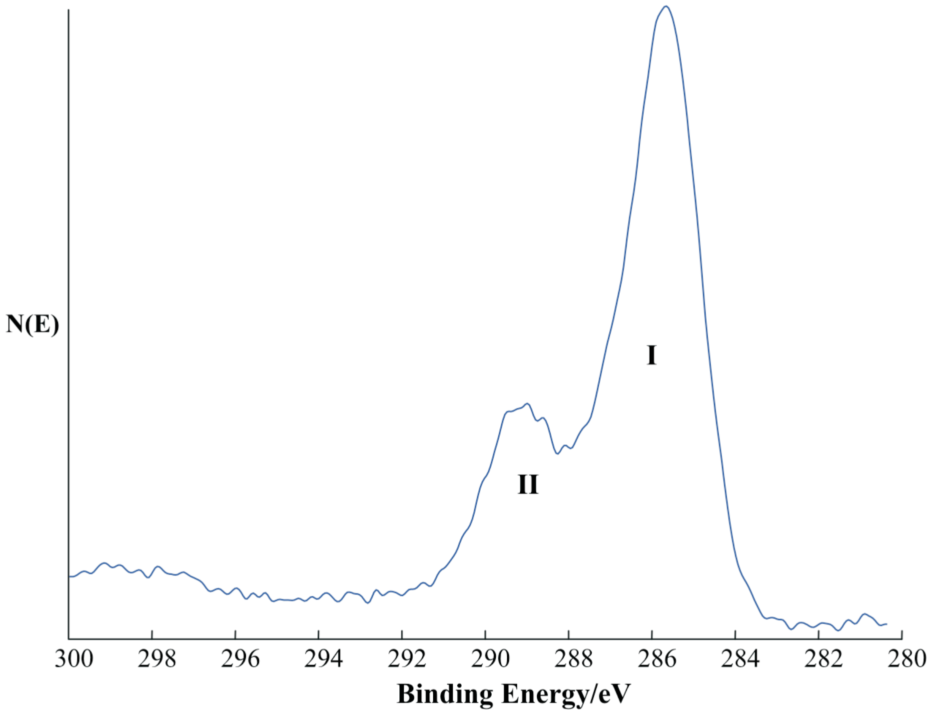

Figure 4 XPS C 1s peak obtained on a reference steel surface.

using XPS (Figs 5 and 8), respectively. The difference between the two iron compounds was observed in the O 1s peak, where the OH and OOH maximum peak height ratios differed. The peak heights and peak height ratios are summarized in Table 6.

Upon contact with acidic and basic solutions, oxide and hydroxide surfaces may acquire an ionic charge by the following reactions:

Low pH: $\mathrm{Fe(OOH) + 3H^+ \rightarrow Fe^{3+} + 2H_2O}$ (1)
High pH: $\mathrm{Fe(OOH) + OH^- + H_2O \rightarrow Fe(OH)_4^-}$ (2)
Low pH: $\mathrm{Fe(OH)_2 + 2H^+ \rightarrow Fe^{2+} + 2H_2O}$ (3)
High pH: $\mathrm{Fe(OH)_2 + OH^- \rightarrow Fe(OH)_3^-}$ (4)

where Equations (1) and (2) are representative of the basic and acidic reactivities of the oxide, respectively, and Equations (3) and (4) are representative of the basic and acidic reactivities of the hydroxide, respectively.

It is shown (Figs 6 and 7) that the surface modified steel substrates change their wetting properties with acidic and basic water characters. Decreased wetting (increased contact angle) was observed with increased pH on the reference sample and better wetting (decreased contact angle) was observed with increased pH on the warm water treated sample. For the reference sample, it is postulated that hydrogen ions adsorb on the Fe(OOH) surface, and contribute to a Fe(II)/Fe(III) oxidation/reduction process (reaction (1)). The number of Fe(OOH) species on the surface decreases with increasing pH (reaction (2)), forming $\mathrm{Fe(OH)_4^-}$ species in a basic medium. It is known that Fe(OOH) species were characterized as having a Lewis acid character[26] and therefore $\mathrm{Fe(OH)_4^-}$ species seem to contribute to

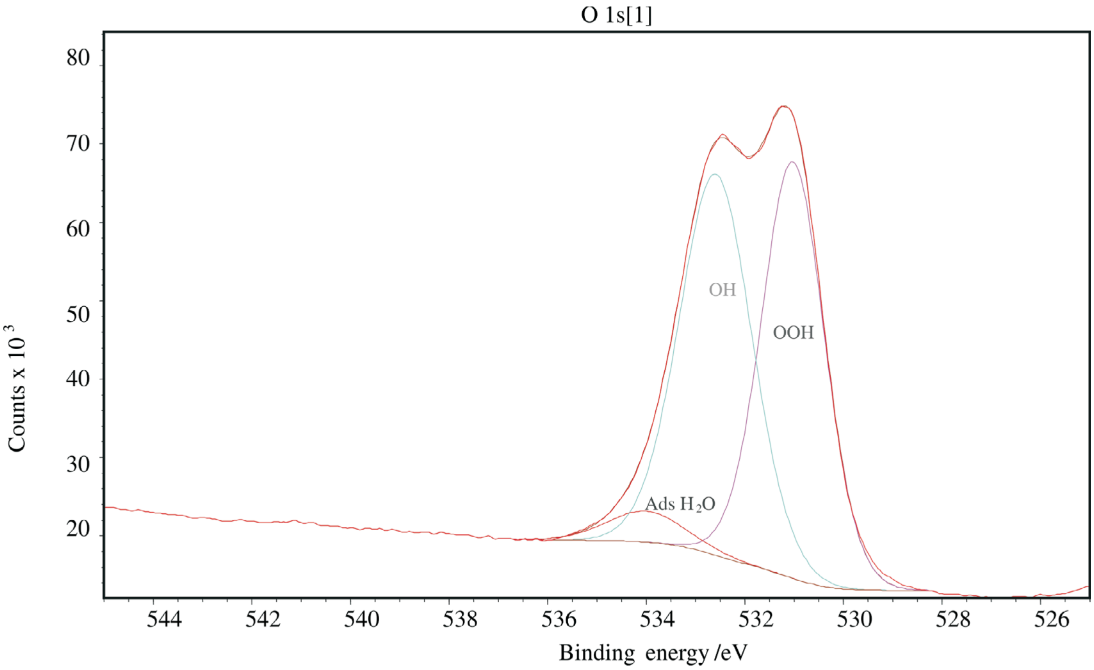

Figure 5 XPS O 1s peak obtained on a reference steel surface.

Table 5 The assignments of the O 1s binding energies (eV) to the surface species for the other samples. All values are in eV.

	Chemical surface species		
	Adsorbed water (H_2O)	Hydroxide [$Fe(OH)_2$]	Metal oxide [$Fe(OOH)$]
Reference	534.00	532.58	531.01
Warm water	534.08	532.40	531.01
Formic acid	534.76	532.99	531.06
Non-formic acid	–	532.54	530.97

Table 6 An estimated correlation determined between $Fe(OH)_2$ and Fe(OOH) peaks.

Name	Binding energy/eV	Chemical surface species	Reference % height	Warm water % height	Formic acid % height	Non-formic acid % height
O 1s	534	H_2O	4.238	3.556	17.153	–
O 1s	532	$Fe(OH)_2$	49.175	78.064	36.651	52.243
O 1s	531	Fe(OOH)	46.587	18.380	43.195	47.243
	Ratio	$Fe(OH)_2/Fe(OOH)$	1.05	4.2	0.84	1.1

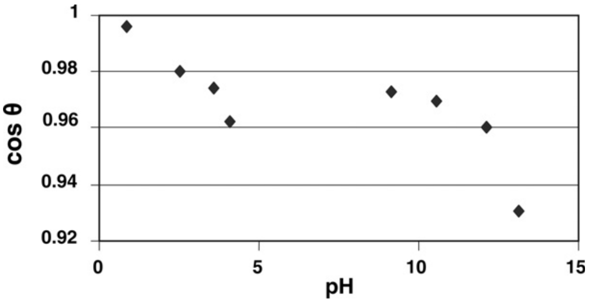

Figure 6 The acid-base contact angle curve of the reference LCAK steel.

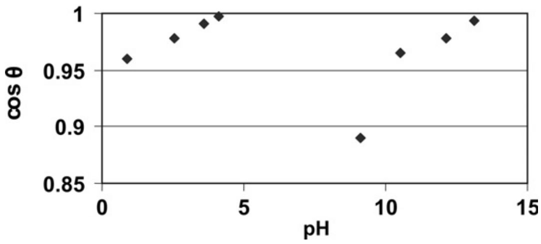

Figure 7 The acid-base contact angle curve of the warm water treated LCAK steel.

a Lewis base character.

The $Fe(OH)_3^-$ species seem to increase on the surface with an increase in pH, lowering the contact angle which gives good wetting properties. $Fe(OH)_3^-$ species seem to have Lewis acid character and $Fe(OH)_2$ species have Lewis base character. The increased concentration of observed $Fe(OH)_2$ species on the surface of the warm water treated sample exhibit Lewis base character, resulting in better wetting (decreasing contact angle) with increasing pH. The results indicate that the wettability measurements predict a basic reactivity for reference LCAK, and an acidic reactivity for warm water treated LCAK.

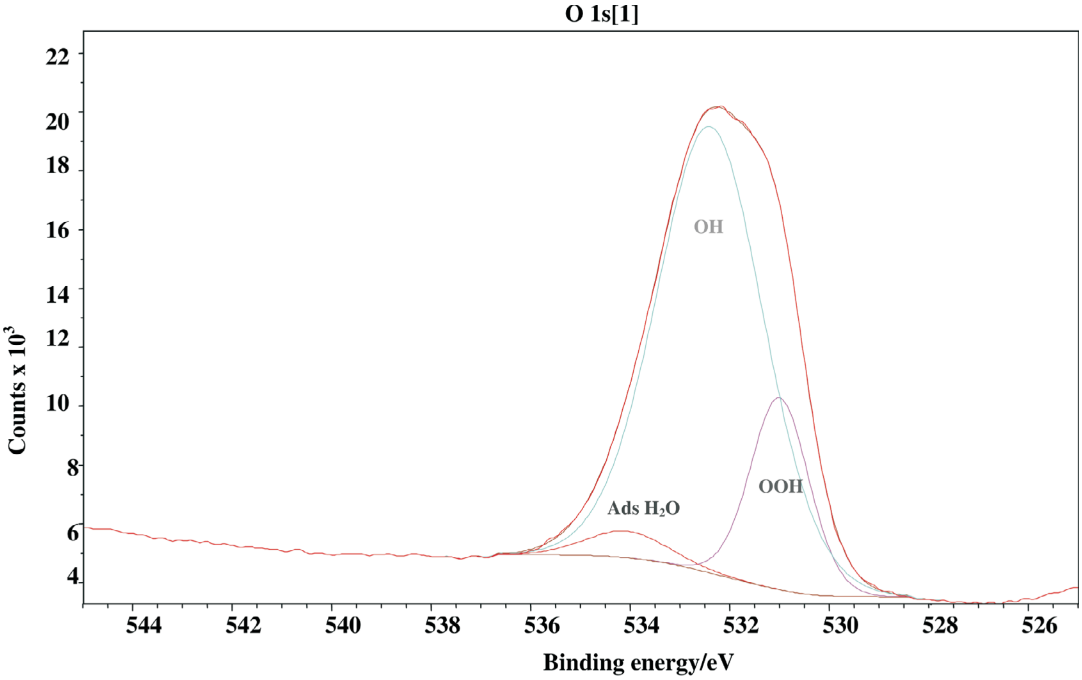

Figure 8 XPS O 1s peak obtained on a surface treated with warm water.

4. Conclusions

As expected from theory, liquids with low surface tension produce low contact angles, thus favouring complete wetting of the surface.

An oxide with Fe(III) dominating on the outer surface formed on LCAK steel in contact with water containing higher/saturated oxygen content, while an oxide with Fe(II) dominating on the outer surface formed in water containing a lower oxygen content. It was also found that the 'oxide films' produced during different treatments behave oppositely during wetting with water solutions containing acidic and basic characters.

The XPS (adsorption) studies showed Lewis-acid properties of standard LCAK steel and Lewis-base properties of the steel surface treated with warm water, while contact angle (wettability) measurements with acidic and basic solutions showed Lewis-base properties for standard LCAK steel and Lewis-acid properties for steel surfaces treated with warm water.

Contact angle and XPS measurements could be used to characterize industrially produced steel surfaces. Low carbon aluminium killed steel surfaces could be modified to be compatible with the chemical characteristics of the paint.

Acknowledgements

The authors express their gratitude to Mittal Steel South Africa for supplying us with substrate material. P.J. Mohlala thanks IMMRI for the use of their instruments. Financial support from the University of Pretoria is gratefully acknowledged.

References

1 R.H. Yoon, T. Salman and G. Donnay, *J. Colloid Interface Sci.*, 1979, **70**, 483–493.

2 F.W. Fowkes, *Ind. Eng. Chem.*, 1964, **56**, 40–52.

3 F.W. Fowkes, *J. Colloid Interface Sci.*, 1968, **28**, 493–505.

4 V. Gutmann, *The Donor-Acceptor Approach to Molecular Interactions,* Plenum Press, New York, U.S.A., 1978, p. 90.

5 A.W. Adamson, *Physical Chemistry of Surfaces,* 5th edn., Wiley, New York, U.S.A., 1990, pp. 107–131.

6 J. Israelachvili, *Intermolecular and Surface Forces,* 2nd edn., Academic Press, San Diego, U.S.A., 1992, pp. 116–133.

7 J.H.E. Fox, *An Introduction to Steel Selection. Part 1. Carbon and Low-Alloy Steels*, Oxford University Press, Oxford, U.K., 1979, pp. 25–27.

8 R.F. Kern and E.S. Manfred, *Steel Selection: A Guide for Improving Performance and Profits*, Wiley, New York, U.S.A., 1979, pp. 114–129.

9 D.A. Elliott and S.M. Tupholme, *An Introduction to Steel Selection. Part 2. Stainless Steels,* Oxford University Press, Oxford, U.K., 1981, pp. 5–15.

10 F.W. Fowkes, *J. Adhes. Sci.Technol.*, 1987, **1**, 7–27.

11 C.J. van Oss, M.K. Chaudhury and R.J. Good, *Chem. Rev.,* 1988, **88**, 927–941.

12 Ref. 5, pp. 385–386.

13 A.R. Balkenende, H.J.A.P. van de Boogaard, M. Scholten and N. P. Willard, *Langmuir,* 1998, **14**, 5907–5912.

14 E. Chibowski and R. Perea-Carpio, *Adv. Colloid Interface Sci.*, 2002, **98**, 245–264.

15 P.M. Costanzo, R.F. Giese and C.J. van Oss, *Acid-base Interactions: Relevance to Adhesion Science and Technology,* (K.L. Mittal and H.R. Andersson, eds.), VSP BV, Utrecht, the Netherlands, 1991, pp. 135–143.

16 F. Pinzari, P. Ascarelli, E. Cappelli, R. Giorgi and S. Turtu, *Appl. Surf. Sci.*, 2000, **156**, 1–8.

17 M. Kimura, H. Ishuguro and K. Tsukahara, *J. Phys. Chem.,* 1990, **94**, 4106–4110.

18 L. Carrino, W. Polini and L Sorrentino, *J. Mater. Process. Technol.,* 2004, **153–154**, 519–525.

19 M. Reffass, R. Sabot, C. Savall, M. Jeannin, J. Creus and P. Refait, *Corros. Sci.,* 2005, **48**, 709–726.

20 J. Dickson, G. Gupta, T.S. Horozov, B.P. Binks and K.P. Johnston, *Langmuir,* 2006, **22**, 2161–2170.

21 L. Carrino, G. Moroni and W. Polini, *J. Mater. Process. Technol.,* 2002, **2–3**, 373–382.

22 F. Garbassi, M. Morra and E. Occhiello, *Polymer Surfaces from Physics to Technology,* Wiley, New York, U.S.A., 1998, pp. 161–199.

23 J.C. Bolger, *Adhesion Aspects of Polymeric Coatings* (K.L. Mittal, ed.), Plenum Press, New York, U.S.A., 1983, p. 3.

24 H.P. Boehm, *Angew. Chem., Intern. Ed. Engl.,* 1966, **5**, 533–544.

25 L-K. Chau and M.D. Porter, *J. Colloid Interface Sci.,* 1991, **145**, 283–286.

26 T. van S. von Moltke and R.F. Sandenbergh, *J. S. Afr. Inst. Min. Metall.,* 2003, **103**, 633–640.