WETTABILITY OF METALLIC OXIDES. APPLICATION TO ADHESION

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ABSTRACT

The various components of the surface energy of SiO$_2$ taken as a model oxide were experimentally determined using low temperature wettability experiments in a two-liquid configuration. Moreover a special attention is paid to the comparison between the surface charges deduced from electrocapillarility measurements and those obtained by direct A.F.M. measurements. Then an analysis of results in terms of acid-base interactions is proposed and extended to AISI 304 stainless steel surfaces with various surface treatments. The ability of these surface treatments to optimize the adhesion energy of AISI 304 / Epoxy joining is finally discussed.

INTRODUCTION

In this paper experimental determinations of the various components of the surface energy of a model oxide such as SiO$_2$ are presented. The obtained results appear to be characteristic of the non-reactive interfaces encountered in many technological areas such as electronics, optics or metal / polymer joining.

These experimental approaches are based on the decomposition into independent terms of the surface energy $\gamma$, as proposed by Fowkes [1] and Good and Van Oss [2]:

i) $\gamma^D$ the dispersive component (characteristic of the Van der Waals long-range interactions),

ii) $\gamma^{AB}$ the acid-base component (characteristic of the short-range interactions).

The expression of the work of adhesion at a solid / liquid interface between a solid oxide and an aqueous solution becomes:

\[
W_{SW} = W_{SW}^D + W_{SW}^{AB} \\
W_{SW} = 2.(\gamma_S^D \cdot \gamma_W^D)^{1/2} + W_{SW}^{AB}
\]

Following Schultz et al. [3], the dispersive component of the surface energy of the solid, $\gamma_S^D$, and the acid-base component of the work of adhesion, $W_{SW}^{AB}$, can be experimentally achieved using a two-liquid wetting technique. For this analysis, contact angles of water droplets surrounded by
an inert liquid are measured on the oxide surface for various inert alkanes such as heptane or octane.

The first part of the paper is devoted to wettability measurements. The basic equations, required for the results analysis, are summarized and the experimental set-up is described. The obtained results concerning the effects of pH of aqueous solutions on SiO₂ surface energy and on the surface charges of silica σ (determined from electrocapillarity measurements) are briefly discussed.

In particular the decomposition of the acid-base part of the work of adhesion in a Brönsted and Lewis contribution is presented.

In the second part of the paper, A.F.M. measurements are presented and the measured surface charges, at a microscopic scale, are compared with those previously obtained.

In the third part, such analysis is applied to compare different surface treatments of AISI 304 stainless steel, these surface treatments being performed in order to optimize the adhesion energy of AISI 304 / Epoxy joining.

1-WETTABILITY MEASUREMENTS

Principle of the method and experimental set-up

As illustrated in Fig.1, the surface energy of an oxide can be deduced from the contact angle of a water droplet lying on this surface and surrounded by an inert hydrocarbon liquid (typically alkanes of various chain lengths). According to the literature [3], this configuration is well adapted to high surface energy solids.

At the solid-hydrocarbon interface, Fowkes analysis [1] leads to the equation:

\[ \gamma_{sh} = \gamma_s + \gamma_H - 2\left(\gamma_s^D \cdot \gamma_H^D\right)^{1/2} \]  
(2)

where \( \gamma_s \) and \( \gamma_s^D \) stand respectively for the surface energy of the solid and its dispersive component and, due to the non-polar character of the hydrocarbon, \( \gamma_H = \gamma_H^D \).

Similarly, at the solid-water interface:

\[ \gamma_{sw} = \gamma_s + \gamma_w - 2\left(\gamma_s^D \cdot \gamma_w^D\right)^{1/2} - W_{sw}^{AB} \]  
(3)

At the equilibrium, Young's relationship is written:

\[ \gamma_{sh} = \gamma_{sw} + \gamma_{wh} \cdot \cos \theta \]  
(4)

The introduction of eq.(2) and eq.(3) in eq.(4) gives the following equation:

\[ \gamma_w - \gamma_H + \gamma_{wh} \cos \theta = 2\left(\gamma_s^D\right)^{1/2} \cdot \left(\gamma_w^D\right)^{1/2} - \left(\gamma_H\right)^{1/2} + W_{sw}^{AB} \]  
(5)
By using series of different alkanes, $\gamma_s^D$ and $W_{SW}^{AB}$ can be deduced from the slope and the intercept at the origin of the straight line obtained by plotting the left hand side of eq.(5) versus the known quantity $\left\{ \left( \gamma_w^D \right)^{1/2} - \left( \gamma_s^D \right)^{1/2} \right\}$.

**Fig 1**: Contact angle in a two-liquid configuration.

Contact angle measurements were performed using an optical Krüss goniometer. Each contact angle reported value corresponds to the average of about 20 measurements with a quasi-gaussian distribution. Surface and interface energy parameters of the different alkanes used in this work and of water are summarized in Table 1.

**Table 1**: Surface and interfacial energies of liquids in mJ m$^{-2}$ [5].

<table>
<thead>
<tr>
<th>Alkanes</th>
<th>$\gamma_H$</th>
<th>$\gamma_{WH}$</th>
<th>Water</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hexane</td>
<td>18.4</td>
<td>51.1</td>
<td>$\gamma_w = 72.6$</td>
</tr>
<tr>
<td>Heptane</td>
<td>20.3</td>
<td>51.0</td>
<td>$\gamma_w^D = 21.6$</td>
</tr>
<tr>
<td>Octane</td>
<td>21.3</td>
<td>51.0</td>
<td>$\gamma_w^{AB} = 51$</td>
</tr>
<tr>
<td>Decane</td>
<td>23.4</td>
<td>51.0</td>
<td></td>
</tr>
<tr>
<td>Dodecane</td>
<td>25.35</td>
<td>51.2</td>
<td></td>
</tr>
<tr>
<td>Hexadecane</td>
<td>27.1</td>
<td>51.3</td>
<td></td>
</tr>
</tbody>
</table>

Wettability results on SiO$_2$

Before any wettability measurements, the roughness of the studied SiO$_2$ surfaces was measured with an interferometer. The obtained values, ranging between 1 and 2 nm, were low enough to be sure that the sample roughness has no effect on the measured equilibrium contact angles [4].

The studied silicon dioxide surfaces were obtained by thermal oxidations of silicon single crystals.

On each sample, XPS investigations based on the analysis of the C1s, O1s, and Si2p peaks were systematically performed. The main characteristics of the oxide layer are an oxide thickness of 6.5 nm covered by a carbon layer 0.2 nm thick and a Si$^{4+}$/O$^2-$ ratio of 0.48.
Equation (5) was plotted for various alkanes using aqueous droplets with different pH. The experimental results are presented in Fig. 2 for pH values of 5.85 and 11.4.

\[ \gamma_{W}^{D} = 86 \pm 14 \text{ mJ/m}^2 \]

\[ \text{pH} = 11.4 \quad W_{SW}^{AB} = 100 \pm 1 \text{ mJ/m}^2 \]

\[ \text{pH} = 5.85 \quad W_{SW}^{AB} = 90 \pm 1 \text{ mJ/m}^2 \]

**Fig. 2:** Experimental results obtained in two-liquid configuration for two different aqueous solutions pH on silica surface. (20°C ± 2).

The variation of the acid-base work of adhesion \( W_{SW}^{AB} \) with the pH is deduced from such experimental curves and plotted in Fig. 3. The experimental point at pH 4 is deduced from an independent experiment with a particular series of alkanes, giving a \( \gamma_{S}^{D} \) value close to 110 ± 10 mJ/m\(^2\). The change of the contact angle with the pH of the aqueous solutions in the two-liquid experiments is reported in Fig. 4.

**Fig. 3:** Evolution of the acid-base work of adhesion measured in a two-liquid experiment with the pH of the aqueous droplets on silica surface.

**Fig. 4:** Change of the contact angle as a function of the pH of aqueous solutions on silica surface in a two-liquid configuration with octane (20°C). pzc is the pH corresponding to zero surface charge.
Discussion of the wettability experiments

The experimental points, presented in the Fig2, align on two parallel lines confirming that $\gamma^D_S$ has a constant value. This means that the dispersive component of the work of adhesion $W^D_{SW}$ is independent of the pH of the aqueous solutions.

On the other hand the variation of the acid-base work of adhesion, $W^{AB}_{SW}$ with the pH, presented in Fig.3, exhibits a parabolic shape.

The total work of adhesion, deduced from the Dupré definition can be written:

$$W_{SW} = (\gamma_S - \gamma_{SH}) + (\gamma_W - \gamma_{WH}) + \gamma_{WH}(1 + \cos \theta)$$

(6)

where $\gamma_{WH}$ (respectively $\gamma_{SH}$) is the interfacial tension between the hydrocarbon H and the aqueous solution W (the solid surface S).

Previous experimental results showed that neither $\gamma_W$ nor $\gamma_{WH}$ are modified by adding small quantities of mineral acids or bases [6]. A simple pH dependence of $W_{SW}$ can then be deduced from equation (6):

$$\frac{dW_{SW}}{dpH} = \frac{dW^{AB}_{SW}}{dpH} = \gamma_{WH} \frac{d \cos \theta}{dpH} = -\frac{d\gamma_{SW}}{dpH}$$

(7)

So, using previously obtained results on the variation of $\gamma_{SW}$ with the pH of the aqueous solution [6], two expressions of the acid-base work of adhesion can be written depending on the surface charge:

i) when the pH of the aqueous solution is close to the point of zero charge (pzc) of the oxide:

$$W^{AB}_{SW} = (W^{AB}_{SW})_{pzc} + 4C \frac{RT}{K} (pzc - pH)^2$$

(8)

with 1/K the Debye screening length and C the aqueous solution concentration.

ii) when the surface charge is close to its maximum value $\sigma_{max}$, the variation of the acid-base work of adhesion is linear with respect to the pH variation:

$$\frac{\Delta W^{AB}_{SW}}{\Delta pH} = 2.3 \frac{RT}{F} 2.2 \sigma_{max}$$

(9)

with F the Faraday constant.

Classically, the acid-base work of adhesion is split in two contributions: a Brønsted contribution, which is pH dependant and a Lewis contribution:

$$W_{SW} = W^D_{SW} + W^L_{SW} + W^{Br}_{SW} (pH)$$

(10)

The results deduced from eq. (7), (8) (9) and (10) are summarized in the Fig.5.

The results obtained on the silica surfaces in a two-liquid configuration are in agreement with those reported in the literature [7]: a pzc value close to 2.5 is found with a negative surface charge for the whole pH range.
In this case the right side of the theoretical curves is only considered since pH keep values higher than the pzc. The maximum surface charge, calculated at the inflexion point of the curve $\theta = f(\text{pH})$ near pH 11 is $\sigma = -8.4 \, \mu\text{C/cm}^2$.

![Diagram](image)

**Fig 5:** On the left, the theoretical evolution of the interfacial tension $\gamma_{\text{SW}}$ with the pH of the aqueous droplets. On the right, the corresponding theoretical evolution of the work of adhesion with the pH.

The conclusion of this first part of the work is that the experimental measurements of the change of the interfacial tension or of the acid-base work of adhesion with the pH lead to the determination of characteristic parameters of the surface oxide namely the pzc and the surface charge.

**2-AFM MEASUREMENTS OF SURFACE CHARGES**

**Experimental procedure**

The same SiO$_2$ samples were also tested using A.F.M. experiments. A microscope Autoprobe CP (Park Scientific Instruments) was used to measure forces versus distance in a liquid cell. At the extremity of the cantilever, a Si$_3$N$_4$ tip with a mean curvature R=50 nm was used.

The three pH investigated (3; 5.7 and 11) were obtained with KCl additions to maintain a constant ionic strength ($10^{-3}$ mol.l$^{-1}$). The force was measured on several points of the surface. For each pH, five curves were recorded and calibrated using a standard procedure. After an averaging procedure the final curve is obtained [10].

The interactions existing between two oxide-like materials in an aqueous electrolyte are described by the classical DLVO theory (Derjaguin, Landau, Verwey, Overbeek). Two types of interactions are involved:

i) the Van der Waals dispersive interactions,

ii) the electrostatic interactions between the two double layers existing at the surface of the materials and resulting from the acid-base dissociation of surface sites (M-OH).
For large distances \((D > 5 \text{ nm})\) the electrostatic interactions are dominant. They are given by the following equation [8]:

\[
F_{el} = \frac{2\pi \varepsilon \sigma \sigma_R}{\varepsilon_0} \left\{ \left( \sigma_1^2 + \sigma_2^2 \right) \exp \left( \frac{-2D}{\lambda_D} \right) + 2\sigma \sigma_0 \exp \left( \frac{-D}{\lambda_D} \right) \right\}
\]  

(11)

with \(\varepsilon\), the electrolyte relative permittivity, and \(\varepsilon_0\) the vacuum absolute permittivity.

\(\lambda_D\) the Debye screening length,

\(\sigma_1\) and \(\sigma_2\) the surface charges of the Si3N4 tip and the SiO2 surface

\(R\) the radius of the sphere which approximates the shape of the tip.

A.F.M. results on SiO2

The experimental results are presented in Fig.6b. For comparison purposes, the change of the contact angles of aqueous droplets on SiO2 with their pH, in a two-liquid configuration, is recalled in Fig.6a.

The curves obtained at pH=3 and pH=5.7 are completely flat, indicating negligible electrostatic interactions between the two substrates. On contrary, at high pH (11) a significant electrostatic interaction is observed between the tip and the silica surface, with an exponential decrease with the distance \(D\).

![Graph showing influence of pH on contact angles and force-distance curves.](image)

**Fig 6:** Influence of the pH on:

a) the contact angles obtained on SiO2 surface in a two-liquid configuration with octane.

b) the force-distance curves deduced from A.F.M. measurements on SiO2 surface with a Si3N4 tip.

A clear electrostatic repulsion is observed only at high pH, indicating a negative surface charge of silica in agreement with the surface charge deduced from the slope \(d\theta/dpH\) on the graph a.

The first tested pH (pH=3) is close to the pzc of silica (pzc=2.5) and corresponds to a negligible surface charge of silica producing no electrostatic interactions with the Si3N4 tip. Similarly, the surface charge of Si3N4 is negligible at pH=5.7 which is very close to the pzc value of this material (pzc=6)[9]. Again no electrostatic interactions between the tip and the substrate were evidenced.
At pH=11, a clear electrostatic repulsion is observed corresponding to similar surface charges on the two materials. By fitting the experimental curve with the equation (11) the following values were obtained: $\lambda_d=23\text{nm}$, $\sigma_i=-0.4\ \mu\text{C/cm}^2$ and $\sigma_s=-2\ \mu\text{C/cm}^2$

Comparison between A.F.M. and wettability measurements

The A.F.M. results are in good agreement with those obtained by wettability experiments on oxide surface. Indeed, the A.F.M. value of the surface charge, -2 \( \mu\text{C/cm}^2 \) has the same sign and the same order of magnitude than the surface charge deduced from the slope $d\theta/dpH$ of the wettability experiment -8.4 \( \mu\text{C/cm}^2 \).

The pzc corresponds to the pH which minimizes the solid-liquid work of adhesion. For pH < pzc a positive surface charge is found, whereas for pH> pzc a negative surface charge is measured indicating a Br"önsted acid-base contribution to the work of adhesion.

3-APPLICATION TO METAL / POLYMER JOINING

Metal / polymer joining is strongly governed by the acid-base interactions existing between the oxide surface of the metal and the polymer. In the last part of this paper, the previous approach, validated on SiO$_2$, is used to analyze in terms of acid-base interactions the consequences of various surface treatments performed on the metallic substrate before the formation of the metal / polymer interface. The studied system is an AISI 304 stainless steel / epoxy joining for which the adhesion energy has been measured by wedge test experiments.

A great number of experimental studies have already been performed on 304 stainless steel surfaces in the as received state, i.e. in a contaminated state, after a plasma treatment of 10 min at 50W, i.e. in a decontaminated state, and in a plasma treated and heated state (200°C, 10 min) [10]. The contact angle variations with the pH of an aqueous solution on these 3 surface states are gathered in Fig.7.

![Fig 7: Contact angle variations with the pH of aqueous droplet on AISI 304 specimens for three surface states: as received, decontaminated and decontaminated + thermally treated.](image)
The contaminated state reveals a nearly constant value of the contact angle, indicating that the acid-base properties of the surface are shadowed by the carbon contamination.

After the heat treatment, the slope of the experimental curve, characteristic of the surface charge, is observed to decrease, signifying a decrease of the hydroxyl form on the surface. In addition, after the heat treatment, we measure a shift of the pzc to a more acidic value. These points are in agreement with XPS measurements. In particular the decrease of the OH form is measured on heated samples and simultaneously the oxidation of the iron rich outer-layer Fe II → Fe III (which is a Lewis acidic form) is clearly observed by XPS experiments [10].

To complete these observations the adsorption of the probe molecule decylamine (DAM) on stainless steel was measured by IR spectroscopy in order to follow the acid-base behaviour change with surface treatment. This probe contains both Lewis and Bronsted basic sites, which are able to react with the corresponding surface sites and giving distinct peaks (the Lewis δNH₂ peak stands at 1610 cm⁻¹ and the Bronsted vC-N peak stands at 1080 cm⁻¹). The intensities of the two peaks obtained on the tested surface states are gathered on Table 2.

**Table 2: Decylamine reactivity vs surface treatments on AISI 304 in regards to the Lewis and Brønsted acid-base properties. Low (+), medium (++) and high (+++) adsorption.**

<table>
<thead>
<tr>
<th>Treatment on AISI 304</th>
<th>Adsorption signal intensity of DAM</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>vC-N 1080 cm⁻¹(Lewis)</td>
</tr>
<tr>
<td>Contaminated</td>
<td>+</td>
</tr>
<tr>
<td>Decontaminated</td>
<td>+++</td>
</tr>
</tbody>
</table>

Adsorption of DAM reveals a pronounced increase of Lewis surface sites on the AISI 304 decontaminated sample.

The influence of these acid-base property changes on the mechanical behavior of stainless steel AISI 304/epoxy joints was tested using wedge test experiments performed in a hot and wet environment. The results of these tests are presented in Fig.8. The polymer used in these experiments was a standard epoxy (DGEBA) with a basic hardener similar to the probe molecule. In this test the quasi-interfacial propagation of the failure was measured according to the exposure time [11]. The adherence energy, which is deduced from this test, is directly proportional to the adhesion energy.

The lower crack propagation associated with the higher adherence energy, i.e. the best behavior, is obtained for the decontaminated + heat-treated surface. The decrease of the number of Bronsted sites (number of hydroxyl sites) is clearly balanced by the increase of the number of Lewis sites resulting from the heating treatment (oxidation Fe II → Fe III).

**4-CONCLUSION**

Experimental determinations of the various components of the surface energy of a model oxide
Fig 8: Crack length vs time for wedge tests of AISI 304 / epoxy joints with different surface treatments

SiO$_2$ are presented and discussed. The acid-base work of adhesion is decomposed in a Bronsted component, which is pH dependant and a Lewis component. In addition, the surface charges deduced from electrocapillarity measurements are in qualitative agreement with those obtained by direct local A.F.M.measurements. Applications of such analysis in terms of acid-base interactions are presented in the case of various surface treatments of AISI 304 stainless steel. These surface treatments are performed to optimise the adherence energy of AISI 304 / Epoxy joining. The heating treatment induces a decrease of the number of Bronsted sites and an increase of the number of acid Lewis sites with a global positive effect on the adhesion energy of stainless steel with a polymer containing a basic hardener.

References