On the respective effect of the surface energy and micro-geometry in the cleaning ability of bare and coated steels

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Abstract

It is aimed in this paper to assess the respective effect of surface energy and topography in the cleaning kinetics of soiled surfaces. Different flat and engraved stainless steels are characterized using contact angle measurements, topographic analysis and cleaning kinetics in presence of surfactants. Two coatings are also distinguished: silicon oxide (hydrophilic) and polysiloxane (hydrophobic).

Except for the engraved surfaces, the determining parameter for the cleaning ability is the polar component of the surface energy: the larger this component, the better the cleaning performance. We proposed a simple model following which favorable interactions take between polar sites and the heads of surfactant. However, for engraved surfaces, the cleaning kinetics is strongly modified by some impregnation phenomena.

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1. Introduction

Soiling stainless steel surfaces is commonplace in the catering industry [1], medical appliances [2,3], food industry [4] and wall panels of buildings [5]. This surface soil can be a favorable environment for further bacterial development. Cleaning is then a point of major importance as far as material performances are considered.

Stainless steels have found widespread use because of their corrosion resistance [6] particularly to aggressive cleaning products. These alloys are protected against corrosion by Cr enriched nanometric oxide films [7,8]. On such “passive” surfaces, various topographies can be obtained by mechanical and/or chemical treatments. Despite these differences, the range of surface energetics for such materials is however relatively restricted, and their surfaces can be considered as fairly hydrophilic [9–11]. In order to strongly modify the energetics of stainless steel, it is then necessary to use non-metallic coatings. To obtain hydrophobic surfaces, one can deposit polysiloxane coatings, using, for instance, chemical vapor deposition (CVD), which are known to be water and oil repellent [12]. To obtain hydrophilic surfaces, one can prepare silicon oxide coatings also manufactured by CVD [13].

To assess the cleaning properties of a material, there are various empirical tests using natural exposure at a long term [5], apolar black soiling for simulating soiling building in urban environments [14], oils [15,16] and removal of pathogenic micro-organisms for food industry [17,18]. On flat stainless steel, the ease of cleaning is generally discussed in terms of passive film composition [19] or surface topography [20]. Nevertheless, there is not yet any comprehensive knowledge on the relevant parameters controlling this surface functionality.

It is intended in this work to assess the respective effect of surface energy and topography in the cleaning kinetics of soiled steel surfaces. In this view, we selected different flat stainless steels and coated stainless steels.
stainless steel surfaces and coatings. The physical chemistry of the surfaces was characterized by contact angle measurements and topographic analysis. The ease of cleaning of these materials was evaluated by measuring cleaning kinetics in a laminar flow cell after an oil spray or an oil film deposit.

2. Materials and methods
2.1. Selection of materials

Some SS30400 (Unified Number System) type 1 mm thick stainless steel sheets, with different surface conditions referred as to Ss1–Ss6, were considered (Table 1).

The final surface condition depends on the finishing process. Stainless steel cold-rolled sheets were generally heat-treated to attain suitable mechanical properties. Bright annealing condition (Ss1) means that the final annealing is performed in a hydrogen-containing atmosphere and does not need any subsequent chemical pickling. However, the residual water content in the atmosphere is sufficient to form a passive film [21]. At the opposite, when this annealing is performed in oxidizing atmosphere, a final pickling is carried out in order to remove the oxide scale (Ss2). Then, the film formation is completed by water rinsing and further exposure to an ambient (water-containing) atmosphere.

Textured surfaces (Ss3 and Ss4) are obtained by using textured work rolls at the end of the cold rolling process. Ss3 is obtained from an initial (Ss2) sheet processed with a final one-directional polished roll. Ss4 is obtained from an initial (Ss3) sheet processed with a final shot penned roll. The chemical attack (Ss5) was performed on a (Ss2) sheet immersed for 10 min in a 60% HNO3 solution with at current density of 120 mA/cm². Mechanically grinding (Ss6) is obtained from an initial (Ss2) sheet processed in industrial conditions using abrasive strip with carbide particles.

Some polysiloxane and silicon oxide coatings were also performed, using plasma assisted chemical vapor deposition (PACVD) with a mixture of O2 and hexamethyldisiloxane (HMDSO) in the reactor chamber. There was an influence of the O2/HMDSO ratio on the physical chemistry of coatings. An increase in O2 led to silicon oxide coatings (PO2/HMDSO = 10). An increase in HMDSO concentration (PO2/HMDSO = 0) induced a polymeric polysiloxane coating. We checked that the composition was homogeneous and measured the coating thickness at 100 nm. Polysiloxane deposits were performed on Ss1, Ss2, Ss3 and Ss5 finishes and referred as to C1, C2, C3 and C4. Silicon oxide deposits were performed on Ss6 and Ss4 surfaces, and referred as to D1 and D2.

Prior to any testing, the test specimens were first soaked in an ethanol/acetone (50/50 v/v) mixture for 5 min, cleaned in an alkaline detergent (RBS 35, Traitements Chimiques de Surfaces, Frelinghem, France) at 50 °C for 5 min at a concentration of 2% (v/v) (pH 10.8). This commercial formulation contained non-ionic and anionic surfactants. Lastly, the surfaces were rinsed five times in distilled water at 50 °C and then five times at room temperature and dried on an absorbent paper.

2.2. Surface free energy of steels

Contact angles (θ) were measured on solid surfaces (S) using a Krüss goniometer G-10, by the sessile drop technique with different pure liquids (L): diiodomethane, formamide and water. After least-squares fitting of the data, the solid surface free energy was estimated by [22]:

\[
\gamma_{S} - \gamma_{L} = \frac{1}{2\gamma_{S}^{1/2}} \left( \frac{\gamma_{L}}{\gamma_{S}^{1/2}} \right) + \frac{1}{\gamma_{S}^{1/2}} \frac{1}{2} \frac{1}{\gamma_{L}^{1/2}}
\]

where γ0 denotes the apolar Lifshitz–van der Waals component and γp is the polar component including ionic, hydrogen, acid–base and covalent interactions.

The solid surface free energy was expressed in mJ/m². Diiodomethane and formamide were provided by Sigma (France) with a purity of 99.5%. Water (milliQ system) was softened and sterile. The energetic characteristics were taken from the literature [23] with γ0 = 50.8 mJ/m² for diiodomethane, 39 mJ/m² for formamide and 21.8 mJ/m² for water and γ0 = 0 for diiodomethane, 19 mJ/m² for formamide and 51 mJ/m² for water. Twenty measurements were performed for each sample.

2.3. Surface topography

The selected parameters were [24] the arithmetic average roughness (Ss) and the maximum peak-to-valley height (Sz) expressed in micrometer. These parameters were deduced from an optical profiler (scans of area 100 μm × 100 μm) using the Surfvision software. In addition, surfaces were also

<table>
<thead>
<tr>
<th>Reference</th>
<th>Surface finish</th>
<th>Fe</th>
<th>Cr</th>
<th>Ni</th>
<th>Mn</th>
<th>Si</th>
<th>Mn</th>
<th>Cu</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ss1</td>
<td>Bright annealing</td>
<td>70.64</td>
<td>17.9</td>
<td>9.05</td>
<td>1.32</td>
<td>0.48</td>
<td>0.15</td>
<td>0.10</td>
</tr>
<tr>
<td>Ss2</td>
<td>Pickling</td>
<td>71.84</td>
<td>18.0</td>
<td>9.12</td>
<td>0.22</td>
<td>0.34</td>
<td>0.22</td>
<td>0.26</td>
</tr>
<tr>
<td>Ss3</td>
<td>Textured</td>
<td>71.84</td>
<td>17.9</td>
<td>8.52</td>
<td>1.01</td>
<td>0.32</td>
<td>0.20</td>
<td>0.21</td>
</tr>
<tr>
<td>Ss4</td>
<td>Chemical attack</td>
<td>71.84</td>
<td>18.0</td>
<td>9.12</td>
<td>0.22</td>
<td>0.34</td>
<td>0.22</td>
<td>0.26</td>
</tr>
<tr>
<td>Ss5</td>
<td>Mechanical grinding</td>
<td>70.65</td>
<td>18.0</td>
<td>8.56</td>
<td>1.86</td>
<td>0.42</td>
<td>0.22</td>
<td>0.27</td>
</tr>
</tbody>
</table>
observed by using scanning electron microscopy with a secondary electron mode.

2.4. Assessment of the cleaning properties

Prior to cleaning, the surfaces were soiled by the nutritious sunflower oil (Lesieur, France) mainly composed of fatty acids (13%), monounsaturated fatty acid (oleic acid) (22%) and polyunsaturated acids (65%), either by oil spraying or oil film deposition with an applicator (Erichsen, Westfalen, Germany). In the first case, the surfaces were covered by a lot of small droplets with a diameter not exceeding 1 μm. It was verified that the droplet repartition was uniform on the sample, leading to a soil density of 0.70 mg/cm² (±0.15). In the second case, the soiling density ranged between 7 and 8 mg/cm² with a thickness of 120 μm.

Surface cleaning was then performed using a laminar flow cell, the details of which are presented elsewhere [25]. This cell consisted in two flat plates between which a commercial detergent (Procter & Gamble) (pH 8.2 at 20 °C) at a final concentration of 1.2% (v/v) circulated, the bottom being the sample to clean[26] . It contains anionic surfactants (less than 5%) and non-ionic surfactants between 5 and 15 wt%.

Based on weight difference, one determines the percentage of oil removed after 10 s (\(R_{10}\)), 20 s (\(R_{20}\)) and 30 s (\(R_{30}\)) of cleaning.

3. Results

3.1. Physical chemistry of metallic and coated surfaces

As illustrated in Fig. 1, the smoothest material is the bright annealed one (Ss 1). Textured (Ss 3) and mechanically grinding (Ss 6) surfaces show some unidirectional lines. Last, three surfaces (Ss 2, Ss 4 and Ss 5) are engraved at grain boundaries.

Contact angles and surface free energies derived from these measurements are presented in Table 2. Stainless steel surfaces are fairly hydrophilic. The water contact angles vary from 37° to 70°. The dispersive component γ\(_d\) is roughly constant. At the opposite, significant variations are observed on the polar components, which range from 11 mJ/m\(^2\) for Ss 2 to 34 mJ/m\(^2\) for Ss 5.

The silicon coated surfaces referred as to D 1 and D 2 are (water contact angles = 11° and 14°) found very hydrophilic: the \(\gamma_p\) components were, respectively, 35 and 36 mJ/m\(^2\). Last,
the polysiloxane coatings (C₁–C₅) are hydrophobic (water contact angles from 96° to 120°).

3.2. Effect of the surface polarity

As shown in Fig. 2, the removal of oil droplets after 10 s of cleaning (R₁₀) is larger than 95% on silicon oxide coatings and smaller than 10% on polysiloxane ones. Whatever the cleaning time, R is larger on flat surfaces (C₁ and Ss₁) than on engraved ones (C₂ and Ss₂). Whatever the surface, the cleaning performance (expressed by R₁₀) is related to the polar component of the surface energy (Fig. 3). Furthermore, a critical polarity (decreasing with the cleaning time) is evidenced from poor to almost complete cleaning.

When soiling the surfaces with an oil film rather than oil droplets, oil does not completely wet the polysiloxane surface (Fig. 4a) contrasting with the complete spreading on silicon oxide coating (D₁) (Fig. 4b). Furthermore, the cleaning kinetics R₁₀ is faster on the hydrophobic surfaces (Fig. 5).

Finally, it was found that the surface polarity plays a major role as well in the fouling control as for the cleaning performance.

![Fig. 2. Oil removal (%) on stainless (Ss₁ and Ss₂) and coated surfaces after 10 s (grey), 20 s (hachured) and 30 s (white) of cleaning.](image)

![Fig. 3. Relation between the polar component of the surface energy (γₚ (mJ/m²)) and the oil removal (%) for stainless and coated surfaces after 10 s of cleaning (R₁₀). The error bars denote the standard deviation.](image)

![Fig. 4. Surface fouling by oil film. Case of: (a) polysiloxane coating (C₁) and (b) hydrophilic coating (D₁). Similar observations were done on bare stainless steel surfaces.](image)

![Fig. 5. Cleaning kinetics R₁₀ is faster on the hydrophobic surfaces.](image)
3.3. Effect of the surface micro-geometry

The effect of the micro-geometry was assessed by comparing standard surfaces (Ss1, Ss3 and Ss6) and engraved ones (Ss2, Ss4 and Ss5). As previously, the cleaning performance expressed by R30 is related to the polar component of the surface free energy (Fig. 6). For this cleaning time, one notes that all the oil is removed from the more polar standard surface, whereas less than 50% is removed from the better engraved one (Ss4). Last, the standard surface finishes, including unidirectional topographies (Ss3 and Ss6), exhibit much better cleaning ability than engraved ones.

4. Discussion

When soiling is performed by the application of a continuous oil film, different spreading behaviours are observed. Hydrophilic surfaces are completely wetted by oil, whereas large droplets are observed on hydrophobic ones.

A hydrophilic surface is generally defined by its high affinity with water, i.e. showing water contact angle $\theta_w < 90^\circ$. This contact angle is a function of the components of the solid surface energy:

$$\cos \theta_w = \frac{2 \sqrt{\gamma_d W} \sqrt{\gamma_s S} \sqrt{\gamma_p W} - \gamma_W}{\gamma_W}$$

An increase in the dispersive or polar component of the solid surface energy leads then to a decrease in $\theta_w$.

By analogy with the macroscopic behaviour of water, lipophilic and lipophobic surfaces can be considered to explain their ability to oil spreading. We should however note that nutritious oil used in this work can be considered [25] as
A decrease in the dispersive component of solid surface energy induces then an increase in the oil contact angle. Then, the lipophilic/lipophobic behaviour depends only on the apolar character of the solid. Low energy apolar surfaces are favorable to limit soiling by oil. Practically, the oil contact angles measured on metal coated surfaces are found \cite{25} to range between 10° and 40°, corresponding to lipophilic behaviour (defined as \( \theta_w < 90° \)).

On the contrary, it was shown in this work that polar (then hydrophilic) surfaces are favorable for the cleaning ability after soiling (assuming that the experience is carried out on similar initial oil fouling). Fig. 7 shows a possible mechanism explaining the effect of the polarity on the surface cleaning, which can be expressed by:

\[
\gamma_{SO} \geq \gamma_{SL} + \gamma_{LO} 
\]  

where S, O and L denote, respectively, surface, oil and cleaning liquid.

Eqs. (1) and (4) lead to (5)

\[
2 \left( \sqrt{\gamma_p^L} \sqrt{\gamma_p^S} + \sqrt{\gamma_d^L} \left( \sqrt{\gamma_d^L} - \sqrt{\gamma_d^O} \right) + \sqrt{\gamma_d^O} \right) \cos \theta_{dL} - \gamma_d^O > 0
\]

Eq. (5) can be split into a positive term (\( \Gamma_r \)) depending on the polar component of the solid surface (\( \gamma_p^O \)) and a negative one (\( \Gamma_a \)) which is a function of the dispersive component of the solid surface (\( \gamma_d^O \)). Finally:

\[
\Gamma_r + \Gamma_a > 0
\]  

where

\[
\Gamma_r = 2 \left( \sqrt{\gamma_p^L} \sqrt{\gamma_p^L} \right) \left( \sqrt{\gamma_p^O} + \sqrt{\gamma_d^L} \right) \sqrt{\gamma_d^O} - \gamma_d^O
\]

and

\[
\Gamma_a = 2 \left( \sqrt{\gamma_d^L} \sqrt{\gamma_d^L} \right) \left( \sqrt{\gamma_d^O} \sqrt{\gamma_d^L} \right)
\]

To explain the difference observed between hydrophobic polysiloxane and hydrophilic silicon oxide coatings, we propose that the surfactant micelles orient their polar heads towards the solid surface. This enhances their adsorption onto polar surfaces. The surfactant molecules can slide under the oil droplets and thereby easily remove them.

A recent work \cite{27} investigated the dynamics at the three-phase contact zone on glass soiled by an oil droplet and cleaned with a solution containing micelles. There is first the formation of the pre-wetting aqueous film between the glass surface and the oil droplet. This mechanism could be applied to our materials under assessment as a pre-wetting film is rapidly formed on silicon oxide coatings but is slowed down on polysiloxane coatings, due to the lack of polar sites.

As far as surface micro-geometry is concerned, the poorest performance in cleaning kinetics was observed on engraved surfaces S_{s2}, S_{s4} and S_{s5}. On these materials, oil impregnation occurs in the metal grain boundaries that are engraved and then not accessible to the detergent flow. Similar trend was observed on coated engraved surfaces C_2 and C_5. On the apolar materials, where the surface composition and
energetics are similar, the role of the micro-geometry in the cleaning mechanism was then evidenced. However, the surface roughness can disturb the contact angle measurements [28] and the surface free energy derived from these measurements is artificially decreased.

Last, little difference was found in surface energies for the different stainless steel surfaces. Carbon-containing substances easily contaminate high surface energy materials such as stainless steel or silicon-containing substrata. This carbon also modifies the surface energy measurements [29–32]. A more detailed study of the effect of surface micro-geometry, including impregnation phenomena, will be presented in a forthcoming paper.

References