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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.

Keywords: Stainless steel; Coating; Cleaning; Soiling; Oil

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 soiling 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 empiric 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

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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 Ss_1–Ss_6, 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 (Ss_1) 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 (Ss_2). Then, the film formation is completed by water rinsing and further exposure to an ambient (water-containing) atmosphere.

Textured surfaces (Ss_3 and Ss_4) are obtained by using textured work rolls at the end of the cold rolling process. Ss_3 is obtained from an initial (Ss_1) sheet processed with a final one-directional polished roll. Ss_4 is obtained from an initial (Ss_2) sheet processed with a final shot penned roll. The chemical attack (Ss_5) was performed on a (Ss_2) sheet immersed for 10 min in a 60% HNO_3 solution with at a current density of 120 mA/cm^2. Mechanically grinding (Ss_6) is obtained from an initial (Ss_2) 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 O_2 and hexamethyldisiloxane (HMDSO) in the reactor chamber. There was an influence of the p_{O_2}/p_{HMDSO} ratio on the physical chemistry of coatings. A high content in O_2 led to silicon oxide coatings ($p_{O_2}/p_{HMDSO} = 10$). An increase in HMDSO concentration ($p_{O_2}/p_{HMDSO} = 0$) 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 Ss_1, Ss_2, Ss_3 and Ss_5 finishes and referred as to C_1, C_2, C_3 and C_5. Silicon oxide deposits were performed on Ss_1 and Ss_2 surfaces, and referred as to D_1 and D_2.

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]:

$$\gamma_{LV}\frac{\cos\theta + 1}{2(\gamma_L^d)^{1/2}} = (\gamma_S^p)^{1/2}\left(\frac{\gamma_L^p}{\gamma_L^d}\right)^{1/2} + (\gamma_S^d)^{1/2} \quad (1)$$

where γ^d denotes the apolar Lifshitz–van der Waals component and γ^p is the polar component including ionic, hydrogen, acid–base and covalent interactions.

The solid surface free energy was expressed in mJ/m^2. 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 $\gamma_L^d = 50.8$ mJ/m^2 for diiodomethane, 39 mJ/m^2 for formamide and 21.8 mJ/m^2 for water and $\gamma_L^p = 0$ for diiodomethane, 19 mJ/m^2 for formamide and 51 mJ/m^2 for water. Twenty measurements were performed for each sample.

2.3. Surface topography

The selected parameters were [24] the arithmetic average roughness (S_a) and the maximum peak-to-valley height (S_t) 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 1
Chemical analysis (wt%) and surface condition (see text) of the investigated steels

Reference	Surface finish	Fe	Cr	Ni	Mn	Si	Mo	Cu
Ss_1	Bright annealing	70.64	17.9	9.05	1.52	0.48	0.15	0.10
Ss_2	Pickling	71.84	18.0	9.12	0.22	0.34	0.22	0.26
Ss_3	Textured	71.84	17.9	8.52	1.01	0.32	0.20	0.21
Ss_4	Textured	71.40	18.3	8.51	0.96	0.43	0.20	0.20
Ss_5	Chemical attack	71.84	18.0	9.12	0.22	0.34	0.22	0.26
Ss_6	Mechanical grinding	70.65	18.0	8.58	1.86	0.42	0.22	0.27