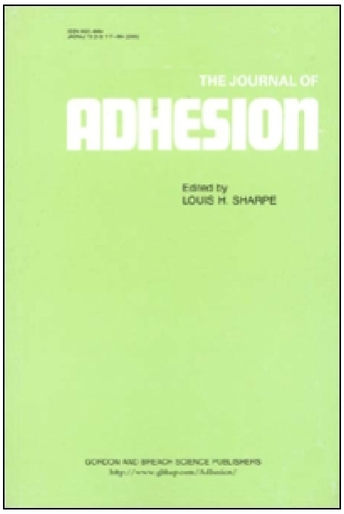

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Adhesion and Wetting Hysteresis of a Metal (Mercury) on an Oxide Glass in Air and Nitrogen*

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In general, oxygen can considerably change the wetting behavior of oxides by molten metals. This work is a basic illustration of the oxidation effect on the wetting behavior of glass by a liquid metal. Taking mercury as a model of a metal, the importance of the metal oxidation in the glass/metal interaction has been observed by measuring wetting contact angles of mercury on glass and the ability of calibrated mercury drops to slide down, under gravitation, on an inclined glass plate in air or in nitrogen. It is believed that the highest force of detachment by sliding of the mercury drop in air results from the metal oxidation which can be interpreted by a higher contact angle hysteresis when the metal is exposed to air.

Keywords: Glass/metal interfaces; wetting; contact angle hysteresis; interface interactions; metal oxidation; mercury

1. INTRODUCTION

Glass/metal interfaces play an important role in many technological applications including glass/metal sealing, metal coatings on glass, float processes, *etc.* In addition, the study of glass/metal interfaces is very attractive from a theoretical point of view because it deals with

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the problem of bonding between two materials that are very different in physico-chemical properties.

The aim of this work is to propose simple methods of study to identify and qualify the molecular interactions existing at glass/metal interfaces.

The literature related to oxide glass/metal interaction is very limited and most of the scientific studies consider only single oxide substrates like SiO_2, Al_2O_3, ZrO_2, MgO [1].

The evaluation of molecular interactions at solid/solid interfaces is a quite difficult problem and there is presently no direct investigative method. The difficulty can be circumvented if one of the two phases (the glass or the metal) can be molten so that the system becomes a liquid/solid interface. In this case, the determination of the energy of interfacial interactions becomes easier, for example, a simple contact angle measurement leading directly to the energy of interactions (reversible work of adhesion) between the two phases.

In this study, mercury has been used as a model of a liquid metal able to develop dispersive and metallic interactions with a solid substrate. Moreover, by taking mercury as a model of metal, the importance of the metal oxidation in the glass/metal adhesion mechanism has been demonstrated by measuring the ability of calibrated mercury drops to slide down, under gravitation, on an inclined glass plate in oxidizing (air) or neutral (nitrogen) atmospheric conditions. It has been observed that the highest force of detachment by sliding of the mercury drop in air results from the metal oxidation which is associated with a high contact angle hysteresis.

2. THEORETICAL–BASIC CONCEPTS IN WETTING

The adhesion energy at an interface formed by bringing into contact two immiscible materials, 1 and 2, can be defined by the work of adhesion, W. This term is the free energy variation per unit area which accompanies the reversible separation of the interface to infinity, and is given by:

$$W = \gamma_1 + \gamma_2 - \gamma_{12} \tag{1}$$

where γ_1 and γ_2 are the surface free energies of phases 1 and 2, respectively, while γ_{12} is the interfacial free energy.

Depending on the combination of materials forming the interface, the nature of the bonding can be significantly different. Such bonds may be physical (van der Waals), metallic, electrostatic, ionic or covalent interactions.

For any immiscible liquid/solid system, the work of adhesion, W, can be calculated from the Young equation involving the liquid surface free energy (surface tension), γ_L, and the Young contact angle, θ_y, at the solid/liquid vapor triple line. This equation is written:

$$W = \gamma_L(1 + \cos\theta_y) \tag{2}$$

assuming, as a first approximation, that liquid vapor adsorption is negligible (this assumption is reasonable with mercury whose partial pressure is only 10^{-3} torr at 20°C). If the liquid vapor adsorption is not negligible, a supplementary term, the spreading pressure, has to be taken into consideration in Eq. (2).

If L is a liquid metal (as mercury), the work of adhesion of the metal on a glass substrate becomes readily quantifiable with Eq. (2).

However, in the general case, the contact angle of a liquid on a solid exhibits a hysteretic feature, two extreme quasi-static values of the contact angle, θ_a and θ_r, being observed, θ_a being the advancing and θ_r the receding contact angles. Contact angle hysteresis may have various origins: surface roughness, modification of the interfacial free energy by physical or chemical processes, heterogeneity of the surface of the substrate, impure liquid (surface tension gradient effects), *etc.*, it has been observed that θ_y, θ_a and θ_r are usually not independent and often satisfy the following approximate equality [2–5]:

$$\cos\theta_y \approx \frac{1}{2}(\cos\theta_a + \cos\theta_r) \tag{3}$$

In this study, the glass/metal interactions will be characterized with these three contact angles, *i.e.*, θ_y, θ_a and θ_r.

3. EXPERIMENTAL

Corning 1737 Liquid Crystal Display (LCD) glass was considered as a solid substrate. The glass was cleaned in an ultrasonic water bath containing a detergent (washed glass). As an option, the impact of a post chemical etching treatment based on a mixture of hydrochloric and hydrofluoric acids was also taken into consideration (etched glass). After cleaning or etching, the glass samples were rinsed in deionized water and dried at 140°C for 30 minutes.

The roughness of the glass substrate was measured by using Atomic Force Microscopy (AFM-I, Digital Instrument). The arithmetic mean roughness, R_a, is equal to 0.17 nm for the detergent-cleaned glass and to 0.42 nm for the acid-etched glass.

Drops of mercury (Hg: 99.9998%, Alfa Aesar) were formed by using a micropipette. Surface tension of mercury, γ_L, was determined with a bubble tensiometer with air or nitrogen and the measured values were found in good agreement with literature data [6] (Tab. I).

The Young contact angle, θ_y, of mercury on LCD glass was measured with 1 or 2 µl sessile mercury drops set on glass samples positioned horizontally inside the environmental chamber of a contact angle goniometer (Ramé-Hart, A-100) at 20°C. The chamber atmosphere was either air at about 50% RH or dry nitrogen (Grade 5 Nitrogen, 99.999% N_2, 1 ppm max. O_2, 1 ppm max. H_2O, 0.5 ppm max. hydrocarbons).

The glass substrates were also supported by a tiltable plane and the tilting angle, α, leading to the sliding under gravity of the mercury drops was noted as a function of the dwell time, δ, of drops on the horizontal substrates (Fig. 1). In this case, drops of mercury having a volume of about 15 µl were formed with a micropipette. The exact mass of mercury of each drop was precisely measured with a microbalance after each sliding test. These sliding experiments were conducted under air (≈50% RH) or nitrogen. In this last case, a plastic box was placed over the glass substrate in which nitrogen circulates and covers the mercury drops at 20°C.

TABLE I Young contact angles (θ_y, degree) in air and nitrogen on 1737 glass (washed and etched). Surface tension, γ_L, of mercury ($mN\,m^{-1}$) in both atmospheres

	Air	*Nitrogen*
γ_L	485.5	489
θ_y(washed glass)	127.5	127.6
θ_y(etched glass)	119.7	122.8

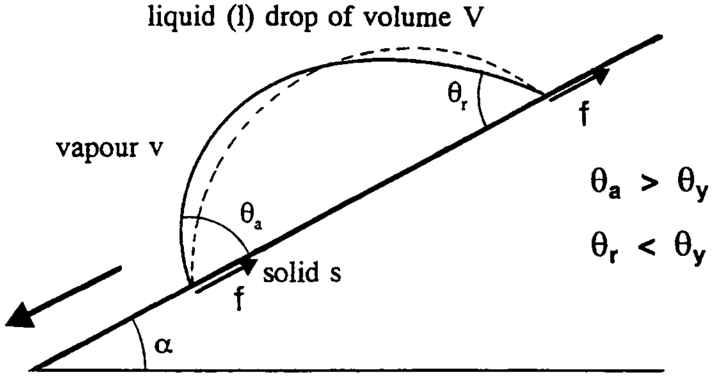

FIGURE 1 Profile of deformed drop (–) corresponding to spherical drop (– – –) sliding under gravity. θ_a and θ_r are the advancing and receding contact angles. θ_y is the Young contact angle of the spherical drop on the horizontal substrate.

4. RESULTS

4.1. Young Contact Angle Measurements

Table I gives the Young contact angle values in air and nitrogen on washed and etched 1737 glass. The mercury surface tension is slightly affected by the nature of the atmosphere and so are the Young contact angles on washed and etched glass. However, the contact angle values are lower on etched glass compared with washed glass. This result may indicate that etched glass interacts more strongly with mercury. From Eq. (2) it can be deduced that:

$$\frac{\Delta W}{W} = \frac{\cos\theta_{y1} - \cos\theta_{y2}}{1 + \cos\theta_{y2}} \tag{4}$$

where subscript 1 refers to etched glass and 2 to washed glass. In air or nitrogen $\Delta W/W$ is close to 0.2 (20%). This conclusion must be weighted by the fact that etching enhances the surface roughness of the glass (Ra increases from 0.17 to 0.42 nm after chemical etching). As roughness increases the contact angles above 90 degrees, the increment of interaction energy, $\Delta W/W$, may be higher than 20%.

Another interesting feature concerning Young contact angles is that they are independent of the residence or dwell time, δ, on the glass substrates, in both atmospheres (air or nitrogen).

4.2. Contact Angle Hysteresis and Sliding of Mercury Drops on Glass

In these experiments, the glass substrates were supported by the tilted plane (Fig. 1), and the tilting angle, α, leading to the sliding under gravity of mercury drops was noted as a function of the dwell time, δ, of drops on the horizontal substrate.

Figures 2 and 3 report the series of experiments conducted in air and nitrogen and present the tilting angle, α, required to produce the sliding of drops on both glass substrates. It increases dramatically with the residence time, δ, in air. The same experiments conducted under nitrogen (Figs. 2 and 3) lead to a very small tilting angle that is constant and independent of the dwell time, δ.

In sliding experiments, when the critical angle, α, is reached, the drop of mercury slides and exhibits, at the front and at the rear of the triple line, the advancing and receding contact angles, θ_a and θ_r (Fig. 1). At the center of the advancing edge Young's equation can be written as:

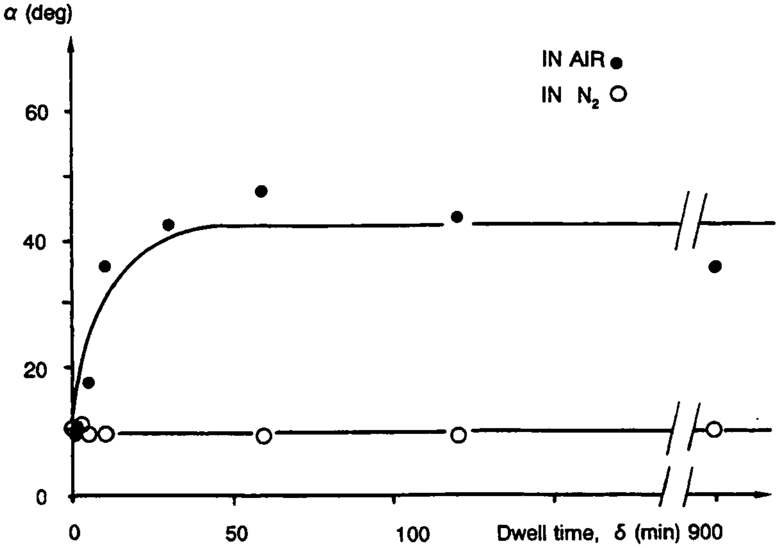

FIGURE 2 Variation with dwell time, δ, of the tilting angle, α, producing the sliding of 15 µl mercury drops, in air (50% RH) and nitrogen. The substrate is washed 1737 glass.

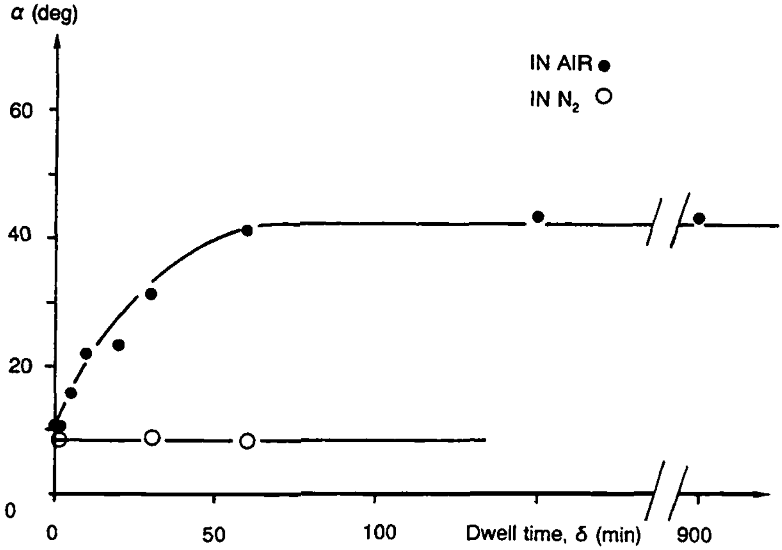

FIGURE 3 Variation with dwell time, δ, of the tilting angle, α, producing the sliding of 15 µl mercury drops, in air (50% RH) and nitrogen. The substrate is acid-etched 1737 glass.

$$\gamma_S - \gamma_L \cos\theta_a - \gamma_{SL} - f = 0 \tag{5}$$

γ_x being the surface free energy of the phase x(solid – S, liquid – L), γ_{SL} the interface free energy between glass and mercury and f is the force resisting movement per unit length of contact boundary. At the center of the receding edge, we have:

$$\gamma_S - \gamma_L \cos\theta_r - \gamma_{SL} + f = 0 \tag{6}$$

and from Eqs. (5) and (6) (which assume γ_{SL} constant) we deduce:

$$f = \frac{\gamma_L}{2}(\cos\theta_r - \cos\theta_a) \tag{7}$$

From Eqs. (3) and (7), it has been demonstrated [3] that a simple relationship exists between the contact angle hysteresis, the sliding angle, α, and the volume, V, of the drop. Assuming that Eq. (3) is reasonably valid, this expression can be written as:

$$V^{2/3} \sin\alpha \approx A(\cos\theta_r - \cos\theta_a) \tag{8}$$

where A is a constant involving the tangent of one-half the Young contact angle $t = \tan(\theta_y/2)$, the density of the liquid, ρ, and its surface tension, γ_L, such as:

$$A = \frac{6^{1/3}\pi^{2/3}\gamma_L}{2t^{1/3}(t^2+3)^{1/3}\rho g} \tag{9}$$

g being the gravitation ($g = 9.81\ \mathrm{m\,s^{-2}}$).

Therefore, experimental results reported in Figures 2 and 3, where α is plotted as a function of the dwell time, δ, can be transformed to show the variation of the contact angle hysteresis, $\cos\theta_r - \cos\theta_a$, of mercury on 1737 glass, as a function of δ. This representation is given in Figures 4 and 5 where $\cos\theta_r - \cos\theta_a$ is plotted as a function of δ for the washed and etched glass substrates, respectively.

Combining Eqs. (3) and (8) allows the calculation of θ_a and θ_r and comparison of these theoretical values with experimental measurements determining directly the advancing and receding contact angles from pictures of the profile of sliding mercury drops. In Table II are gathered the experimental values of θ_a and θ_r in air and the theoretical ones deduced from Eqs. (3) and (8) for the washed glass substrate. We observe a fairly good agreement between the two series of values

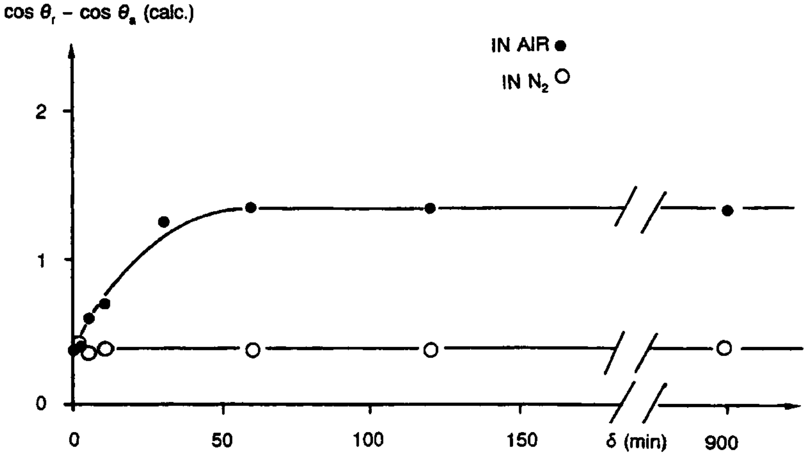

FIGURE 4 Contact angle hysteresis, $\cos\theta_r - \cos\theta_a$, of mercury drop adhering on glass as a function of the dwell time, δ, in air (50% RH) and nitrogen. The substrate is washed 1737 glass.

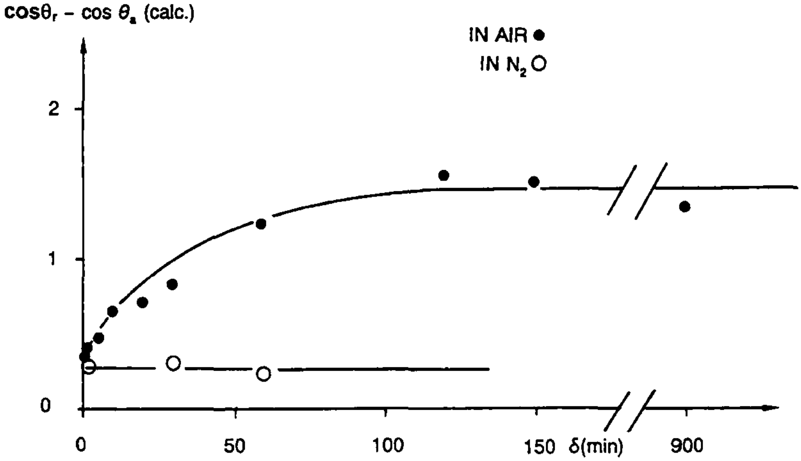

FIGURE 5 Contact angle hysteresis, $\cos\theta_r - \cos\theta_a$, of mercury drop adhering on glass as a function of the dwell time, δ, in air (50% RH) and nitrogen. The substrate is acid-etched 1737 glass.

TABLE II Comparison between calculated (calc) and measured (m) values of advancing and receding contact angles, θ_a and θ_r, in air, of mercury drops set on washed 1737 glass. The dwell time of mercury on glass is δ, in minutes (θ_y = 127.5)

δ	$\theta_a(calc)$	$\theta_a(m)$	$\theta_r(calc)$	$\theta_r(m)$
5	140.5	143.5	116.4	115.0
10	150.6	149.0	110.2	109.5
30	162.2	159.0	105.4	94.0
60	180.0	165.0	95.8	92.5
3600	180.0	165.0	63.2	51.0

In nitrogen: θ_a(calc) = 144.2, $\theta_{r(\text{calc})}$ = 114.1, independent of δ (θ_y = 127.6).

despite a more apparent discrepancy for the high advancing contact angles reaching 180° for θ_a (calc.) and θ_a(m). However, it should be noticed that the cosines of these angles do not differ more than 4%. The increase of the contact angle hysteresis with the dwell time is correlated with an increase of the mercury drop adherence in air. The same behavior of mercury is observed with the etched substrate and the theoretical values of θ_a and θ_r are presented in Table III. In nitrogen, the contact angle hysteresis is small for both glass substrates, the difference between θ_a and θ_r staying around 20 to 30 degrees.

TABLE III Calculated values of advancing and receding contact angles, θ_a and θ_r, in air, of mercury drops set on etched glass as a function of the dwell time, δ, in minutes ($\theta_y = 119.7$)

δ	0.5	1	5	10	20	30	60	120	150	(15 *hrs*)
θ_a	132.9	135.1	137.6	145.8	160.0	156.2	180	180	180	180
θ_r	108.1	106.4	104.6	99.5	92.9	94.4	75.5	55.2	62.5	68.6

In nitrogen: $\theta_a = 133.0$, $\theta_r = 113.7$, independent of δ ($\theta_y = 122.8$).

5. DISCUSSION

A net increase of the sliding angle, α, and, therefore, of contact angle hysteresis of mercury is observed with dwell time in air on both glass substrates. On the contrary, no variation of advancing or receding contact angles was noticed in the presence of nitrogen.

Usually, nitrogen, dry oxygen or dry air do not react with mercury at room temperature (20°C). However, traces of water vapor may produce a slow oxidation of the metal [7]. Therefore, it comes to mind that the main difference between the two series of experiments (air or nitrogen) is that mercury is slowly oxidized in air at 50% RH. This hypothesis is supported by the occasional presence of a stained ring formed around drops of mercury on glass after the longest dwell times in air. It is very probable that this ring is related to mercury oxidation. Furthermore, the specific adsorption of Hg^{2+} ions onto negatively-charged sites of glass surfaces has been also described [8].

The fact that the stained ring is formed only around drops at the solid/liquid/vapor (SLV) triple line may also indicate that the oxidation of mercury is catalyzed by glass, the catalytic oxidation of mercury by impurities (for example some glass components) also being recognized [7].

Figure 6 represents the situation with a mercury drop after a long dwell time in air ($\delta \geq 1$ hr). From the Young equation, we will assume that the solid/liquid interfacial free energy is not the same at the advancing and receding edges. At the advancing edge, we consider that:

$$\gamma_{SL} = \gamma_S - \gamma_L \cos\theta_a \tag{10}$$

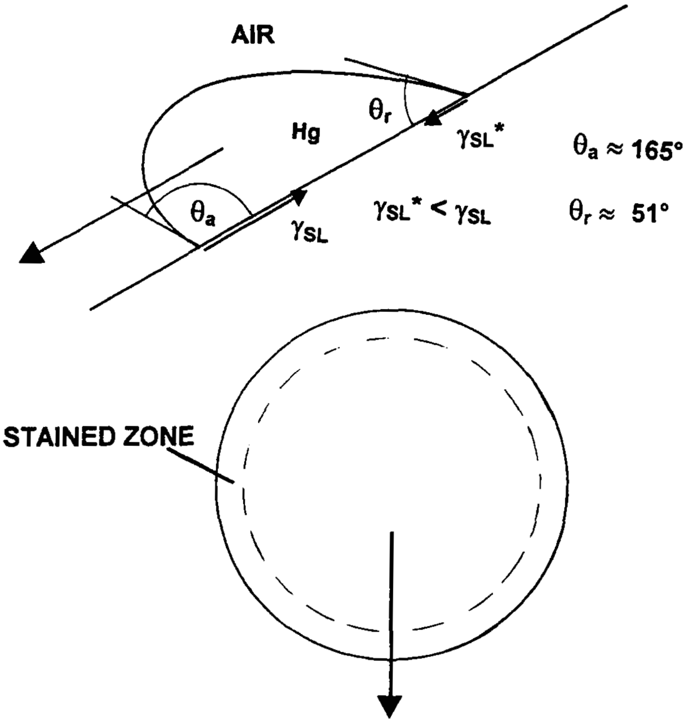

FIGURE 6 Interpretation of the contact angle hysteresis as a variation of the solid/liquid interface free energy due to mercury oxidation in air (50% RH).

and at the receding edge, that:

$$\gamma_{\mathrm{SL}}^{*} = \gamma_{\mathrm{S}} - \gamma_{\mathrm{L}} \cos\theta_r \tag{11}$$

From Eqs. (10) and (11), it follows that:

$$\gamma_{\mathrm{SL}}^{*} - \gamma_{\mathrm{SL}} = \gamma_{\mathrm{L}}(\cos\theta_r - \cos\theta_a) \tag{12}$$

Therefore, the difference, $\gamma_{\mathrm{SL}}^{*} - \gamma_{\mathrm{SL}}$, may be of the order of 800 mJ m^{-2} (mN m^{-1}) when the contact angle hysteresis reaches its maximum value. From the chemical composition of glass, it is possible to estimate its surface free energy [9] which is of the order of 370 mJ m^{-2}. This value allows us to estimate the interfacial free energy at the receding edge, γ_{SL}^{*}, and at the advancing edge, γ_{SL}.

We obtain, respectively:

$$\gamma_{SL}^{*} \approx 65 \text{ mJ m}^{-2}$$

and:

$$\gamma_{SL} \approx 840 \text{ mJ m}^{-2}$$

(for these calculations, we use the θ_a and θ_r values of Tab. II). This analysis is not contradictory to Eqs. (5)–(7). It implies simply that $2f = \gamma_{SL} - \gamma_{SL}^{*}$.

These two different values indicate that the solid/liquid interfacial free energy may be much lower when the SLV triple line moves on the stained ring (receding edge) than when the SLV triple line moves on the unstained glass surface (advancing edge). The respective values of γ_{SL}^{*} and γ_{SL}, and the presence of the stained ring at the SLV triple line, lead us to conclude that mercury is oxidized at the SLV triple line in the presence of air and that the resulting mercury oxide (stained zone) reduces the solid/liquid interfacial free energy. This phenomenon dramatically increases the contact angle hysteresis when the drop starts to move on the stained zone.

The effect of the presence of oxygen on the wettability of pure oxide surfaces by a liquid metal has been extensively studied. An application of this effect has led, for example, to the metal-oxygen technology for the brazing and joining of number of oxide ceramics to metal with a good bond strength [10]. Our observations and deductions corroborate this conclusion.

6. CONCLUSION

With simple experiments of wettability, it has been demonstrated that the adherence of metal (mercury) drops to glass (1737 LCD glass) is greatly increased when the metal is exposed to air. This observation may have numerous practical consequences and applications.

Metal oxidation seems to increase the contact angle hysteresis and, in particular, to reduce the receding contact angle. This mechanism is accompanied with the formation of a stained zone at the SLV triple line and with a reduction of the solid/liquid interfacial free energy.

The measurements of contact angles with mercury sessile drops, on the horizontal substrate, do not reveal the impact of the environment and of the oxidation, the contact angles in the situations being unaffected by the environment (air or nitrogen).

As a general comment, the characterization of wettability with advancing and receding contact angles provides much more information on the solid/liquid interaction mechanisms than the conventional measurement of the Young contact angle. The contact angle hysteresis can be determined with a sessile liquid drop by inclining the substrate and allowing the drop to deform as a function of gravity as shown in this study, or by following the capillary rise of the liquid on a vertical solid plate [11], simply by immersing or withdrawing the vertical solid surface into or from the liquid.

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