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Influence of Experimental Variables on the Measure of Contact Angle in Metals Using the Sessile Drop Method

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Abstract

The sessile drop method is an easy and fast method used to measure the contact angle between solids and liquids. The value of the contact angle is used in surface characterization, in particular the wettability of solid surfaces by the liquid and to calculate the surface free energy. In this work, we study the effects of the volume of the drop placed on the surface, the elapsed time between drop placing and measurement and the cleaning of the substrate (not cleaning, washed with ethanol or washed with acetone) in the value of the contact angle on Ti6Al4V and AISI 316 stainless steel. We found that drop asymmetry is a very important parameter that must be considered in CA measurements. An asymmetry parameter used to qualify the drop asymmetry is proposed. It was also found that the degree of cleanliness produces dispersion in the contact angle values; on the other hand no differences were found between cleaning with ethanol or acetone. CA decreases with time and increases slightly with decreasing droplet volume.

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Keywords: contact angle; sessile drop method; wettability; surface; experimental errors

1. Introduction

Liquids spread over a material in different ways. Wettability is the degree to which a liquid spread over a solid and it may be determined by measurement of the contact angle (CA). This measurement permits, in the case that the liquid is water, to distinguish material surfaces which are hydrophilic or hydrophobic [Lattner et al. (2009)]. Besides,

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the CA could be used to calculate the surface free energy by means of an appropriate mathematical model [Żenkiewicz (2007)].

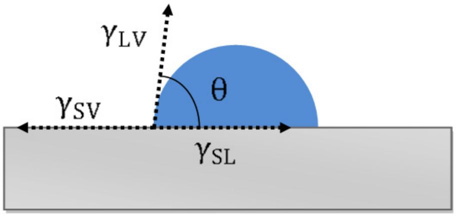

Fig. 1. Schematic of a contact angle of a liquid drop placed on a solid surface.

The most common method to measure the CA is the sessile drop method. In this method a drop of liquid is placed over the surface of the material, forming in this case a system of three phases; solid (solid surface), liquid (drop) and gas (surrounding atmosphere). The three phases create three interfaces: liquid-vapor (drop-atmosphere), solid-liquid (solid material-drop) and solid-vapor (solid material-atmosphere) interfaces. The intersection of the three interfaces form a line called three phase line or contact line [Kwok et al. (1999), Kwok et al. (2000)], see Figure 1. The contact angle is defined as the angle formed by the tangent of the liquid-vapor interface and the solid-liquid interface in the contact line. The physicist Thomas Young proposed a simple equation relating the CA with the interfacial tension of the system, as:

$$\cos\theta = \frac{\gamma^{SV} - \gamma^{SL}}{\gamma^{LV}}$$

where $\gamma^{SV}, \gamma^{SL}, \gamma^{LV}$ are the solid-vapor, solid-liquid and liquid-vapor surface tension, respectively [Kwok et al. (2000)].

Several factors have been reported having an influence in the experimental determination of the contact angle by the sessile drop method and must be taken into account, as follows:

Roughness and chemical heterogeneity of the surface: A sessile drop on a plane, horizontal and smooth solid surface (ideal surface) shows axial symmetry adopting the spherical cap form. An axi-symmetrical drop shows only one angle of contact along the contact line, the invariance of this angle is a characteristic of the liquid, and a property of the system. The chemical heterogeneity and the surface roughness produce deviations of the axi-symmetric form of the drops. The contact angle in that case varies along the contact line, i.e., none contact angle could be assigned to the system [Ruiz Cabello (2009)]. Figure 2 shows examples of a perfect axi-symmetrical drop and also of an irregular drop with a so called ameba-like shape; in the first case there is a unique CA and in the second the CA varies along the contact line.

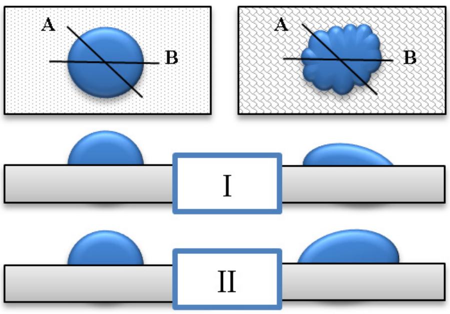

Fig. 2. Types of sessile drops: an axisymmetric drop (left) and non-axisymmetric drop (right).Where I and II are cross section of the planes A and B, respectively.

Superficial impurity: particles or liquids adsorbed on the surface prevent a direct interaction between the liquid and the solid surface, for that reason, the measured CA may not be correct. If the impurity is homogeneously spread on the surface the CA measured will not be the angle of the original solid surface, in the case the impurity is heterogeneously spread, the drop will be asymmetrical. This contamination is commonly associated to procedures followed during cleaning of the surface.

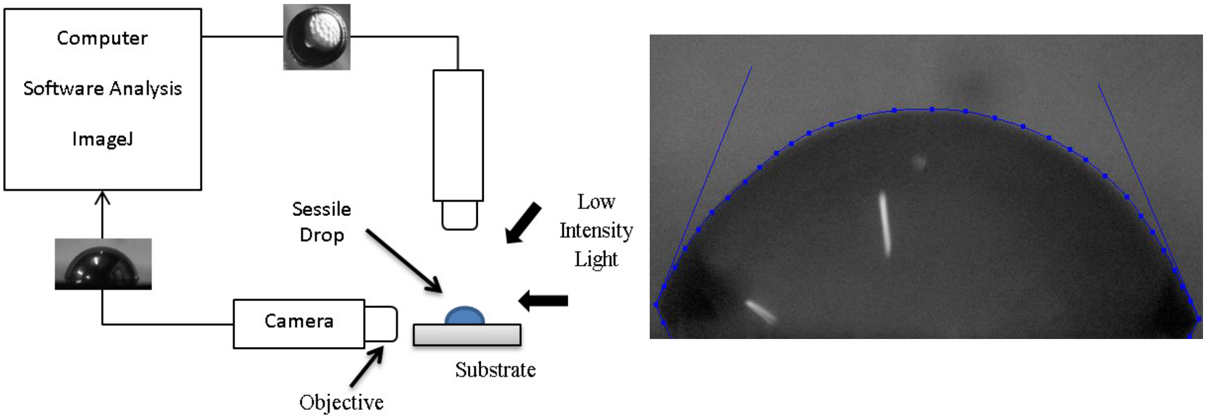

Fig. 3. Scheme of the goniometer, planar and side view of sessile drops (left); and photograph of a drop during measurement of the contact angle in the software ImageJ (right).

The size of the drop: According to the literature, the volume of the drop (drop size) should be in the range between 0.5 and 10 mm^3 [Blythe et al. (1978), Kaelble et al. (1971), Rudawska et al. (2009)]. However, in several reports the volume of the drop is not included. In general, small size drops are used, but the comparison between results obtained with drops of different sizes should include the effect of the drop size.

Time since the deposition: According to Rudawska et al. (2009) the measurement of CA should be made in a short time after the deposition of the drop on the solid surface. The time should be the same for all drops. In that way the volume lost by evaporation and possible reaction of the liquid with the surface will be minimized. The influence of this factor is well explained, but no quantitative analysis was reported on the effect on the CA measurement.

Temperature: Temperatures in the range from 20 to 40 ºC could show little difference in the surface tension of the liquid. For that reason, small changes in temperature have no appreciable influence in the contact angle [Rudawska et al. (2009), Zhao et al. (2004)].

Mechanical vibration: during the measurement, the sample should be static to avoid deformation of the drop due to vibrations.

Liquid reactivity: chemical reaction between the solid and the liquid could interfere in the measurement, for that reason careful analysis should be made before the measurement to avoid erroneous values [Rudawska et al. (2009)].

It is therefore very important that an accurate determination of the CA is necessary to establish reliable surface properties of a given material. In particular it results important the calibration and sensibility analysis of the experimental conditions of the measurement of CA by the sessile drop method. The purpose of the present research is to analyze the effect of the volume of the sessile drop, the time after deposition and the cleanliness of the surface on the results of CA measurement on two materials; Ti6Al4V alloy and AISI 316 stainless steel.

2. Experimental Methods

2.1. Goniometer

The measurement of the CA was performed in a home-made goniometer, which is composed of a microscope, a holder for the sample and a camera, see Figure 3. The measurement procedure was calibrated using hemispherical steel particles with a known contact angle from 50º to 125º. The maximum relative error associated to the whole measurement was less than 5%. The procedure is described in the next section.

2.2. Deposition of the drop and measurement of the contact angle

First, the drop is placed on the surface, then the drop is photographed, and finally the photograph is used to measure the angle.

Before each measurement the sample is cleaned with detergent, rinsed with water, rinsed with ethanol and dried with hot air. The drop is placed, once the sample achieves room temperature, on the material using a graduated syringe to dose a very precise volume of liquid, slowly and carefully to produce a regular and symmetrical drop.

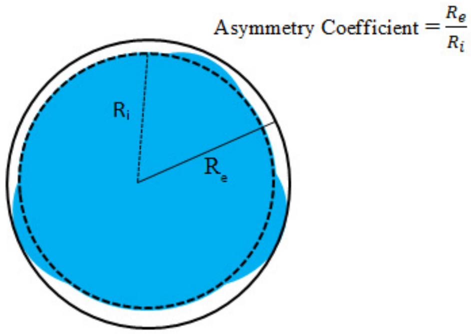

Fig. 4. Schematic representation of an irregular drop viewed from the top (shadow in blue), the full circle is the excircle and the dashed circle is the incircle.

Once the drop is placed on the material a photograph is taken. The photograph is digitally processed and analyzed using the software ImageJ [Rasband (1997–2014)]. Two angles are measured on the photograph: the left and the right angles, both angles and the mean of both are obtained, see Figure 3. In all the cases a symmetry test was performed to assure a single contact angle, the test for symmetry of the drop is described below.

2.3. Test for drop symmetry

To test for symmetry, the photograph of the drop is analyzed observing its view from the top and determining the deviation from a perfect circle by comparison in two steps (see Figure 4); plotting both, the largest circle containing the drop (Excircle) and the smallest circle contained in the drop (Incircle).

The ratio between both radii, the excircle and the incircle, is called the asymmetry coefficient and takes values of 1 for a perfect circle and larger than 1 for imperfect circular drops.

The natural dispersion of the drop on each material was determined in order to identify the degree of asymmetry of the drops, in order to do this several drops were placed on the surface and the asymmetry coefficient was calculated using the ImageJ software [Rasband (1997–2014)].

2.4. Experimental parameter studied

All the tests were performed at room temperature (25 ±3 ºC) using water as the standard liquid test because of its good properties, since it is not adsorbed neither chemically reacts with the materials. In addition, in all the cases the samples were strongly held to avoid movement and vibration. The roughness (Ra) was measured using a profilometer with a spatial resolution of 10 nm, using an RC phase filter with a cut-off of 0.8 mm on a path length of 4 mm. The reported value is the mean of 5 lectures in different places of the surface.

2.4.1. Surface cleaning

Three cleaning conditions were employed: without cleaning, washing with ethanol and washing with acetone. In all cases, the drop volume was between 2 to 5 mm^3 and the time of measurement was 10 seconds.

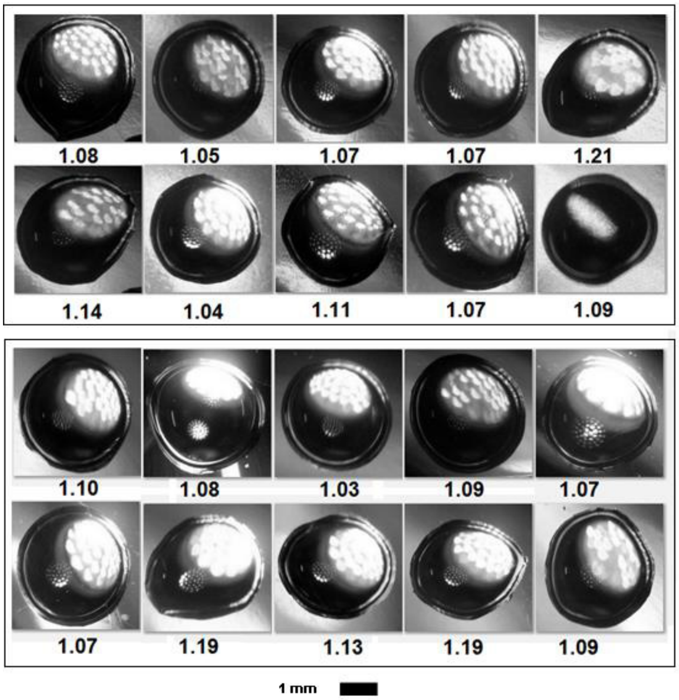

Fig. 5. Water drops placed in the surface material with the symmetry coefficient. Above (10 pictures): Ti6Al4V; below (10 pictures): 316 stainless steel.

-*Without Cleaning:* The surface is washed with detergent, rinsed with water then with ethanol and dried with hot air. Then, the first drop is placed on the surface and the photograph is taken. Before that, the drop is completely absorbed with a paper and no additional cleaning is performed. The following four drops are placed in the same location and the respective photographs are taken.

-*Ethanol Cleaning:* Before the deposition of each drop, the surface is washed with detergent, and rinsed with water, then with ethanol and finally dried with hot air.

-*Acetone Cleaning:* Before the deposition of each drop, the surface is washed with detergent, and rinsed with water, then with acetone and finally dried with hot air.

2.4.2. Drop volume

Drops of water of different volumes were placed on the material. The drop volume is calculated assuming the drop is a spherical cap. 40 drops were placed to analyze the influence of the volume on the contact angle; the volume used range from 1 to 10 mm^3. In all cases, the time of measurement was 10 second and the ethanol cleaning procedure was used.

2.4.3. Time after deposition

The evolution of the drops placed on the materials is followed by measurements performed at 10, 40, 70, 100, 130, 160 and 190 seconds from the time of deposition. Five repetitions of this procedure were performed. In all cases, the drop volume ranged from 2 to 5 mm^3 and the ethanol cleaning procedure was used.

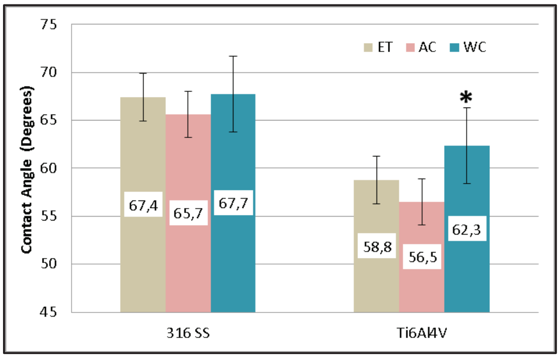

Fig. 6. Contact angle measured with different cleaning treatments. ET: ethanol; AC: acetone; WC: without cleaning. *Ti6Al4V WC treatment shows significative difference faced to ET and AC (t Student test, $P < 0.001$)

2.5. Materials

Two materials were used, Ti6Al4V titanium alloy (6%Al, 4%V, remainder Ti) and AISI 316 Stainless Steel (16%Cr, 10%Ni, 2%Mo, 2%Mn (max), remainder Fe). Both were cut in 1x2 cm plates 0.2 cm in thickness. Besides, the plates were grinded and polished to obtain a low roughness. The titanium alloy samples were grinded using #220 to #1500 SiC papers, then polished with 1 µm diamond slurry and ethylene glycol; and the final polishing was performed using 0.02 µm silica suspension and H_2O_2. The stainless steel samples were grinded using #220 to #2000 SiC papers; and the final polishing was performed using 1 µm diamond slurry and ethylene glycol. It must be mentioned that the surface of the Ti6Al4V samples have a TiO_2 film of about 10 nm formed during the last step of polishing by reaction with H_2O_2.

The mean roughness (Ra) obtained in the titanium alloy samples was equal to 39 ± 10 nm, and in the AISI 316 SS was equal to 48 ± 10 nm.

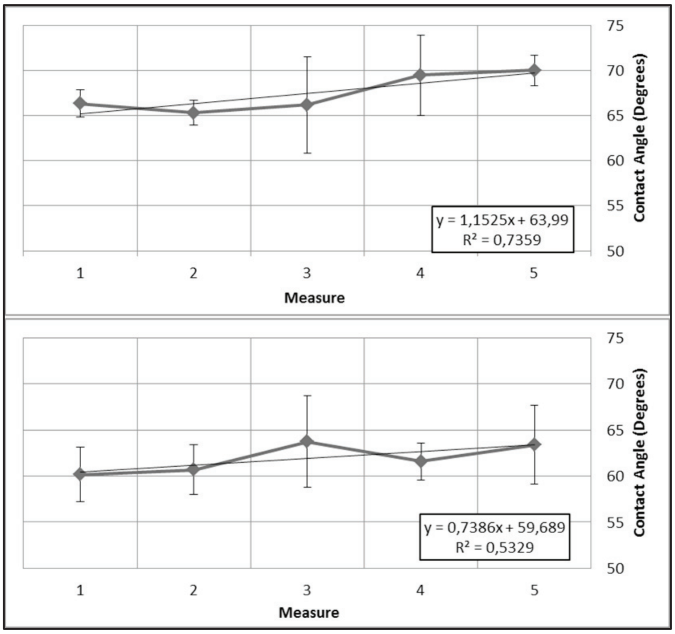

Fig. 7. Contact angle on samples without cleaning, for 5 consecutive drop depositions. Above: 316 SS, below: Ti6Al4V

3. Results

3.1. Drop symmetry

In Figure 5, 10 drops of water placed on titanium alloy samples and 10 drops placed on 316 SS samples are shown. In the figure it is possible to observe that for titanium alloys the asymmetry coefficient is between 1.04 and 1.21 with a mean value of 1.09. In the case of the stainless steel samples the asymmetry coefficient is between 1.03 and 1.19 with a mean value of 1.10.

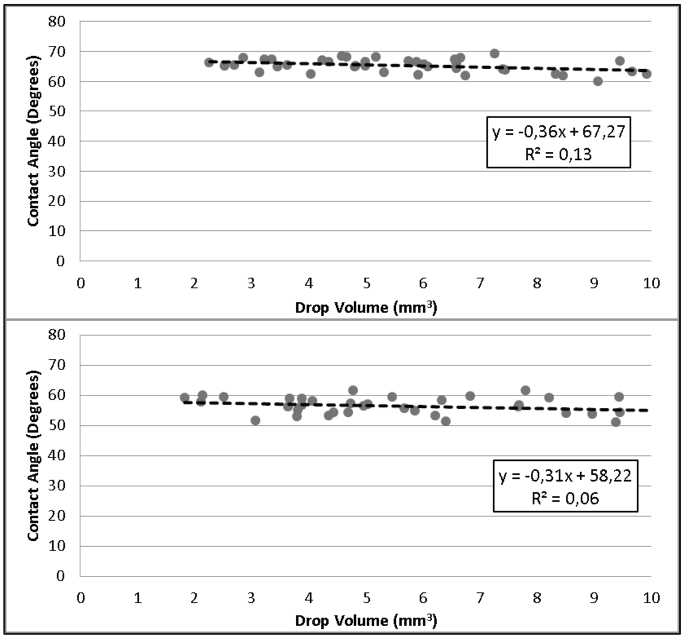

Fig. 8. Contact angle as a function of the drop volume. Above: 316 stainless steel; below: Ti6Al4V.

It may then be assumed that the largest mean deviation for both materials could be given by an asymmetry coefficient value of 1.10. In this case, if any asymmetrical drop is assumed to have an ellipsoidal cap shape with main axis in its base following the same ratio as the drop as shown in Appendix I, the contact angle measured for the real asymmetrical drop will have a dispersion resulting in a maximum of 10% error in the CA measurement. On the other hand, in 70% of the drops shown in Figure 5 the asymmetry coefficient is less than 1.10, therefore it is reasonable to assume that the same probability or dispersion will hold for the side photographs of the drops. Based on the relation between the asymmetry coefficient and its effect on contact angle, the following method for the CA measurement is adopted: first, two pictures of the drop is taken; second, the asymmetry coefficient is determined, if this is less than 1.10, the contact angle is measured and registered for this drop. In this way the dispersion or error will be less than 10 %.

3.2. Surface cleaning

The results of the measurements of CA as a function of the three different cleaning procedures applied on the sample surfaces are shown in Figure 6. In the case of titanium alloys the main observation is that there is no difference between contact angles measured for surfaces cleaned with ethanol or acetone; however in the case of surface without cleaning, the contact angle measured is larger than for the cleaned surfaces. In the case of 316 SS samples, there were no significant differences of the contact angles measured for the three surface conditions.

A very important observation for the case of the drops on surface without cleaning condition in titanium alloy and 316 SS is that all the drops deposited after the first one had asymmetry coefficient larger than 1.10, therefore the

CA measured and reported may have an error larger than 10%. For all these non-first drops the asymmetry coefficient has a mean value of 1.20. Moreover, the value of CA increases as the order of deposition of the drop increases, as can be observed in Figure 7, for both materials. The increase in asymmetry with drop order deposition may be attributed to the adsorption by the surface of impurities present in the non-cleaned surface.

According to these results, it may be concluded that the cleaning procedures with acetone and ethanol permit to obtain reliable results with the degree of expected accuracy, with a relative error estimated in less than 8 %. In the case of the surface without cleaning the relative error was of 15 %.

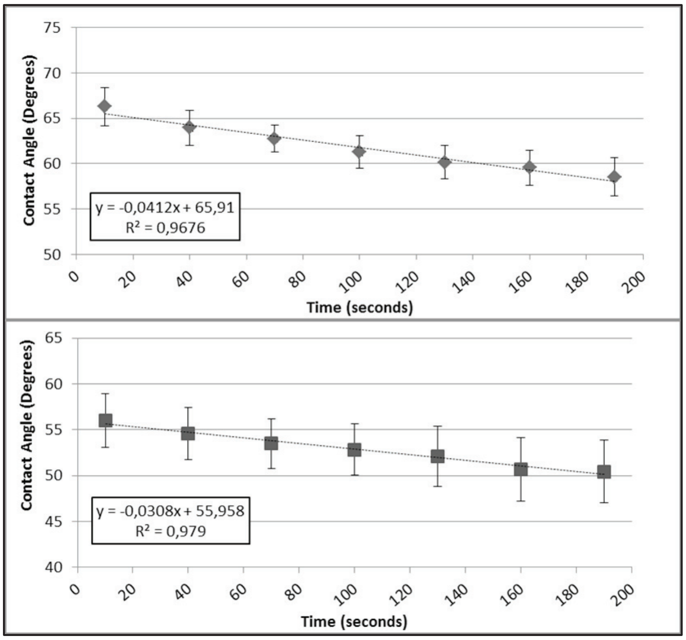

Fig. 9. Contact angle as a function of the time from the moment of drop deposition.
Above: 316 SS, below: Ti6Al4V. The error bars show the experimental dispersion of five in repetitions.

3.3. Drop volume

In Figure 8, the results of contact angle measured as a function of drop volume are shown. On the titanium surface the mean value of the contact angle is equal to 56.5º ± 2.9º and the drop volume ranged from 1.5 to 10 mm^3. On the other hand, on the stainless steel surface the mean value of the contact angle is equal to 65.2º ± 2.2º and the drop volume ranged from 1.5 to 10 mm^3.

In both materials a small decrease in measured contact angle as the drop volume increases was observed. However, this change may be masked by the dispersion in the measurements due to the asymmetry of the drops which creates an uncertainty of about 10% which is the order of the observed changes. In conclusion, from an experimental point of view the drop volume does not affect the CA measurement. However, small drops permit a larger number of repetitions of drop deposition and measurement in one sample placed without cleaning, also small drops are more regular in shape with little deformation, and finally it becomes easier to focus in the microscope smaller than larger drops.

3.4. Time since deposition

In Figure 9 the values of the contact angle as a function of time of measurement after drop deposition are shown in both materials: titanium alloys and 316 SS, both in the cleaning conditions referred as ethanol cleaning. A clear linear decrease in the contact angle with time is observed. For titanium alloys at 10 seconds is 56.0º ± 2.9º and at 190 second is 50.4º ± 3.4º with a decrease of 5.6º ± 0.8º and a rate of change of 1.9º ± 0.3º per minute. In the case of

316 SS the corresponding values are 66.3º ± 2.1º and 58.5º ± 2.1º with a decrease of 7.8º ± 2.8º between 10 and 190 seconds. In this case the rate of change is of 2.6º ± 0.9º per minute, faster than in the case of titanium alloys.

This change could be attributed to the evaporation process and an associated change in drop geometry due to different degrees of anchoring of the contact periphery of the drop onto the substrate surface, which does not modify the wetting surface area in a proportional way to the decrease in volume. This is consistent with the different rates of change of CA between titanium alloy and 316 SS with better wetting of water in the first case.

With practical sense it is reasonable to conclude that a maximum time elapsed after deposition of 10 seconds will maintain the measurements of CA within the error due to dispersion by other effect, rather than exclusively due to a systematic error due to the rate of change of CA with time (see Figure 9).

4. Conclusions

The evaluation of the main experiments conditions on contact angle measurement by the sessile drop method on Ti6Al4V alloys and AISI 316 Stainless Steel has shown the following:

-*Symmetry of the drop:*

Drop symmetry is a very important parameter that must be considered in CA measurements. For a low rough surface, Ra = 39 nm for titanium alloy and 48 nm for 316 stainless steel, approximately only 50 % of the drops present an asymmetry of less than 10%.

Evaluation of drop asymmetry could be performed by optical visualization of the drops from the top.

The first drop placed in any specific site is the most symmetrical, subsequent drops placed in the same site present increasing degree of asymmetry.

Cleaning of the surface with ethanol or acetone is efficient in order to obtain reproducible CA measurements.

-Drop volume:

The value of measured contact angle slightly increases as the drop volume decreases.

The change in contact angle with drop volume (1.5-10 mm^3) is within the dispersion in the measurement by other effects.

Small drops (1.5-5 mm^3) have little morphological changes with subsequent deposition of drops in the same place.

-*Time after deposition:*

The value of contact angle measured as a function of time after deposition decreases with time.

An optimum elapsed time of 10 seconds is considered suitable since the decrease is within the dispersion due to errors by other effects.

The results show that the CA measurements should be made at a fix time in order to compare the effects of other variables and parameters on CA measurements.

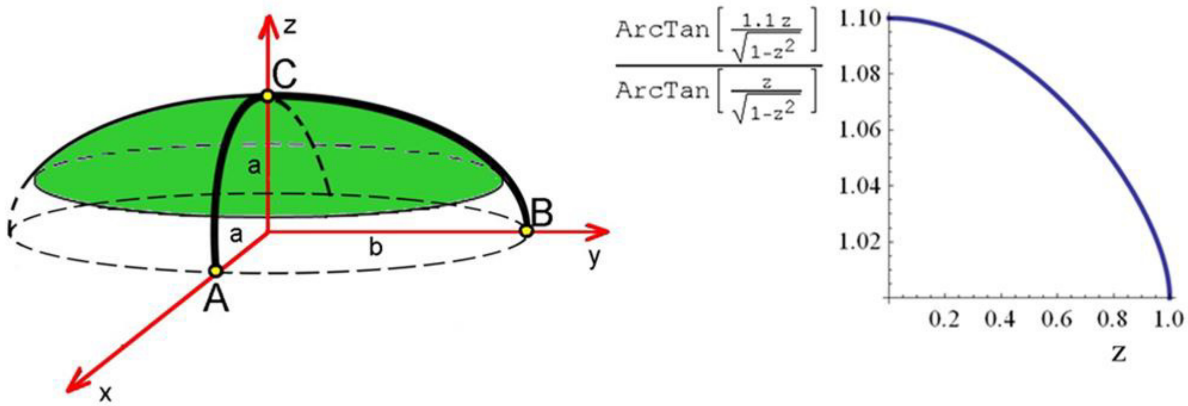

Fig. 10. (a) Model of the ellipsoidal cap drop (the axes are not in scale). (b) Ratio of the extremes angles as a function of z.

Appendix A. Ellipsoideal cap drop

An ideal shape of a drop placed on a surface could be assumed to have a spherical cap geometry. In the present analysis, deviations towards an ellipsoidal cap geometry are assumed and evaluated.

The drop volume occupies only a fraction of any of both cap geometries. For an ellipsoidal drop it could be only the shadow part of the Figure 10(a). For a spherical cap the contact surface is the surface area of a circle of radius r, for an ellipsoidal cap it is the ellipse with main radii a and b. For the spherical cap the contact angle is the same at any point of the triple point, formed by the circumference of the contact circle. In the case of an ellipsoidal cap there are two points where the contact angle is maximum or minimum, respectively, and those are the points A and B in Figure 10(a), which are the points at which the curves AC in the *xz* plane, and CB in the *zy* plane, intersect the axes *x* and *y*, respectively.

The points of curves AC and BC are represented by the following analytical functions f and g;

$$f(z) = \sqrt{1 - z^2}$$
$$g(z) = \frac{b}{a}\sqrt{1 - z^2} \tag{1}$$

being b/a the asymmetry coefficient of the drop.

The slope at any point of curves AC and BC is calculated as the derivative of f and g as a function of *z*; as:

$$f'(z) = \frac{-z}{\sqrt{1-z^2}} \tag{2}$$

$$g'(z) = \frac{-\frac{b}{a}*z}{\sqrt{1-z^2}} \tag{3}$$

The ratio of the angles of the tangent at any point *z* of the curves AC and BC can be calculated as ArcTan (g`(z)) / ArcTan (f `(z))

Now, considering a specific case in which b/a=1.10, the ratio between those angles are as shown in Figure 10(b), as a function of z. It is observed that the ratio varies between 1.0 at z=1 (bottom of the cap) indicating that there is no difference between both angles, and a largest value of 1.10 at z=0, that is the ratio of CA at the triple points A and B. That is, an asymmetry coefficient of b/a=1.10 will give the largest ratio of contact angle of the value (CA)A/(CA)B = 1.10, which shows a direct and equal relation between asymmetry coefficient and the correspondent largest contact angle ratio for an ellipsoidal cap.

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