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International Journal of Heat and Mass Transfer 51 (2008) 4628–4636
International Journal of HEAT and MASS TRANSFER
www.elsevier.com/locate/ijhmt

Contact angle and sessile drop diameter hysteresis on metal surfaces

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Received 11 December 2007

Abstract

The experimental stand to measure the static contact angle and drop diameter is presented in the paper. The results of contact angle and diameter of the drops on aluminium, brass, copper and stainless steel with different roughness are added. The measurements were done for the increasing and decreasing drop volume. As a result the hysteresis of contact angle and magnitude of wetting surface was observed. It was noticed that aluminium and stainless steel lose their hydrophobic properties during the dropping procedure while copper and brass remain the hydrophilic or hydrophobic material.

Keywords: Contact angle; Wetting; Hysteresis; Liquid–gas interfaces; Solid–liquid interfaces; Laser methods

1. Introduction

The wetting phenomena play an important role in the heat and mass transfer processes, e.g., steam generation, heat transfer in two phase heat exchangers, fume scrubbing systems and many others. Wetting properties are defined by the magnitude of contact angle. If the contact angle is lower than 90° material is hydrophilic otherwise it is hydrophobic.

Contact angle may be calculated by the well-known Young equation [1] and this equation is valid for the ideal surface (e.g. flat, rigid, chemically homogenous, non-reactive and insoluble). However, there is no ideally flat and smooth surface in technical conditions. Wenzel [8,9], Cassie [10] as well as Shuttleworth and Bailey [11] proposed the equation in which the average roughness ratio was employed and it is known as the Wenzel equation. More advanced investigations were done by Marmur [5,6] for axisymmetric rough surface and he proposed augmented the Wenzel equation. Further, Marmur took into consideration profiles of the solid surface and liquid-fluid interface. The comparison of the last two equations is made in work [7]. The experimental investigations of contact angle of liquid Al on Al_2O_3 surface for different roughness were made by Zhou and De Hosson [12]. In this work the models of wetting for different grooves' directions were presented. The experimental results of the impact of roughness on contact angle were obtained by Rybnik and Trela [13].

It has been observed that a liquid has two different contact angle magnitudes: higher during drop expansion (so-called advancing contact angle) and lower during drop decreasing (retreating contact angle). That phenomenon is named hysteresis.

The problem of wetting hysteresis was theoretically investigated by Yang [3], who applied the first law of thermodynamics in his research. More detailed attitude to wetting hysteresis is presented by Marmur [4]. He assumed that drop possessed a periodically heterogeneous surface. As a result, it is concluded that equilibrium contact angle is the average of the intrinsic contact angles on both edges of a drop. Since the most experiments were done only for advancing contact angle, the author decided to make experiments considering the hysteresis of contact angle.

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doi:10.1016/j.ijheatmasstransfer.2008.01.027

Nomenclature

d	diameter of a sessile drop	*Greek symbols*	
D	dimensionless diameter of a sessile drop	ρ	density of liquid
g	gravitational acceleration	σ	surface tension
v	volume of the sessile drop		
V	dimensionless volume of the sessile drop		

2. Experiment

The contact angle is not only material property dependent, but it changes with the surrounding conditions, time and it also depends on the history of wetting. Therefore the measurement of contact angle and the wetted area must be very complicated. The impact of above properties results in the hysteresis.

2.1. The experimental set up

In order to investigate the wetting phenomena the author constructed a stand showed in Fig. 1. A sessile drop (1) was photographed by the CCD camera (5) and its diameter and contact angles on two edges were measured in photography by PC (6) with the professional computer code. The diameter was measured in the photography as the length of a line connecting two edges of the drop. The requested temperature of plate's surface (2) was obtained by heating the water in ultrathermostat (17) and pumping it through the double spiral channel made in the heated plate (7). The plates were levelled with geodesic level.

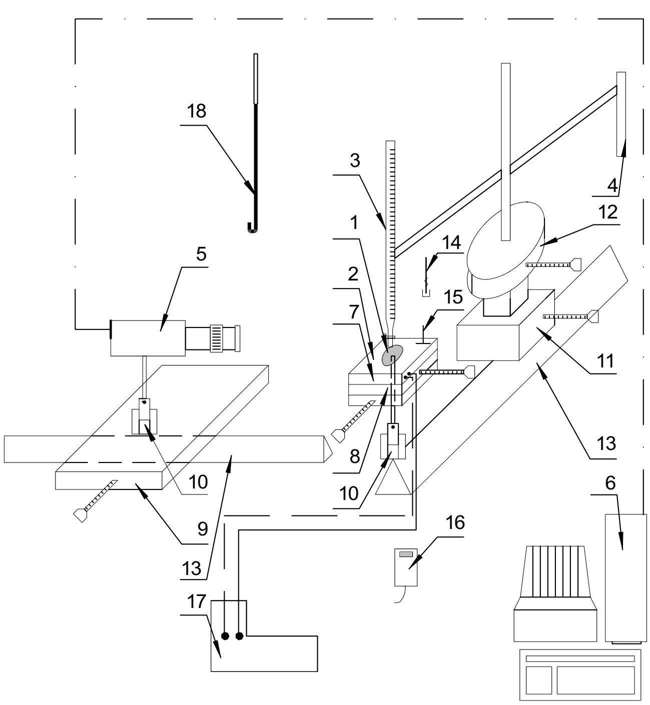

Fig. 1. The experimental stand: 1 – sessile drop, 2 – test plate, 3 – burette, 4 – benchmark of a linear dimension, 5 – CCD camera, 6 – personal computer, 7 – heated plate, 8 – table of precise movement in two horizontal directions, 9 – table of precise horizontal movement, 10, 11 – elements of vertical movement, 12 – rotator, 13 – optical bench, 14 – relative humidity and temperature probes, 15 – resistance thermometer probe, 16 – thermo-hygrometer, 17 – ultrathermostat, 18 – barometer.

The plates were sanded with abrasive paper with the same grit. As a result, a circular roughness geometry was obtained. A new sheet was used for each plate. Each sheet was pressed with the same force against the plate surface. Because each material had different hardness the various roughness had to be obtained.

The sessile drop was photographed applying the shadow method, in which the light fell through the drop on the camera, as an example a photo is presented in Fig. 2.

2.2. Experimental results

Since the hysteresis is one of the properties of the wetting phenomena, the investigations were conducted for the increasing and decreasing volume, which corresponded to advancing and retreating contact angle respectively. The experimental results are presented in the dimensionless form. The dimensionless diameter and volume are obtained from the formulas:

$$D = \frac{d}{\sqrt{\frac{\sigma}{\rho g}}}, \tag{1}$$

$$V = \frac{v}{\left(\frac{\sigma}{\rho g}\right)^{3/2}}, \tag{2}$$

Fig. 2. The sessile drop on the brass plate and the benchmark of a linear dimension above it.

The research was started from the comparison with the known results. As a benchmark, the experiments of Ponter et al. [2] were used. The very good agreement between author's measurements and the benchmark experiments was observed (see in Fig. 3), hence the applied experimental method was verified positively.

2.3. Observations and discussions

The experiments on brass, stainless steel and aluminium are very difficult, because the drops with contact angles about $\pi/2$ are unstable. For that reason, drops became either unsymmetrical or broke down into less drops. Therefore, the measurements in wide range of volume not always were possible.

In spite of the differences in component and roughness of investigated plates, it was noticed that for small dimensionless volume of drops (40 and less) the diameters of drops are very closed. As a result, it can be concluded that for small drops the properties and roughness of solid plate are negligible.

In order to analyse the achieved results more carefully, each experiment is presented in one figure. The changes of contact angle and diameter of a drop are presented together. Letter "S" indicates the start point of experiment.

The contact angle on the copper plates during the enlargement of a sessile drop increased and decreased rapidly. The contact angle changes were similar to oscillations (cf. Figs. 4 and 5). The oscillations were not observed when the water was dropping. The examination of experimental results of contact angle on the copper plate led to the conclusion that the rapid changes of the contact angle and the contact angle differences on both edges were caused by the absence of the first adsorbed layer. According to the BET theory, the first adsorbed layer has the energy of bonds, that can be compared to the energy of chemical bonds. The energy of next layers is like the energy of condensation. The plate was left on the air after it had been sanded down, so different molecules from surrounding air might have been adsorbed. Moreover, the adsorption process might have been unfinished before the experiments, so the investigated surface was not homogenous. As a result, different values of contact angle on both edges were measured. Therefore, the abrupt changes of contact angle were caused by a violent adsorption. Then, after having been sanded down, the plates made of aluminium, brass and stainless steel were immediately immersed into the distilled water for 24 h. When immersing water was adsorbed, the first adsorbed layer remained homogenous. For that reason, the oscillations of contact angle and substantial differences between contact angles on two edges disappeared.

It was noticed that a drop could extend and contact angle could increase simultaneously up to a critical contact angle value, which is different for each material. If the value is exceeded, the drop extends easier and the next contact angle value is significantly smaller. The value of the critical contact angle can be obtained only as a rough approximation because determining the contact angle was not the aim of the presented research. It is about: 1.3 rad for copper, 1.4 rad for aluminium and $\pi/2$ rad for brass. In a dropping procedure the analogous behaviour of a drop was observed only one time, so it might be caused by a measurement error.

When volume is increased the diameter is widened too. However, in some cases, it was observed that the diameter of the drop decreased slightly when the water was added or

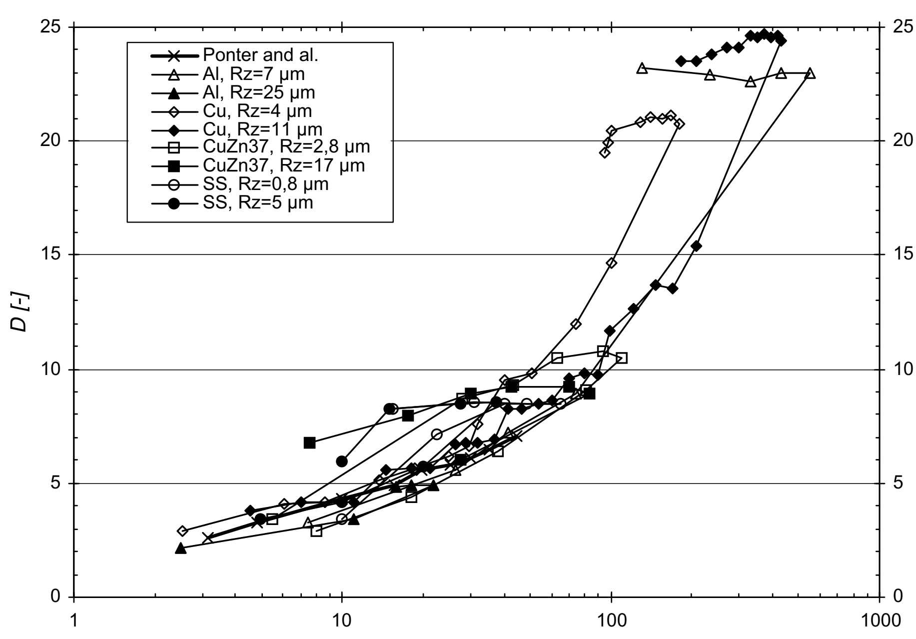

Fig. 3. The presented results compared with Ponter et al. data [2].

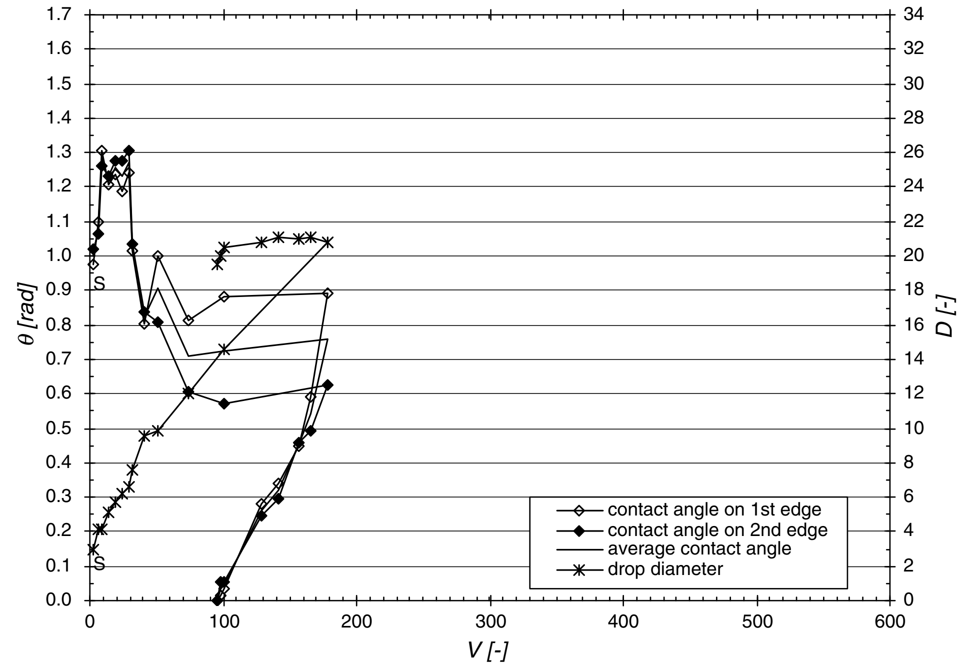

Fig. 4. Contact angle on both edges and diameter of the drop on copper with roughness $R_z = 4$ μm.

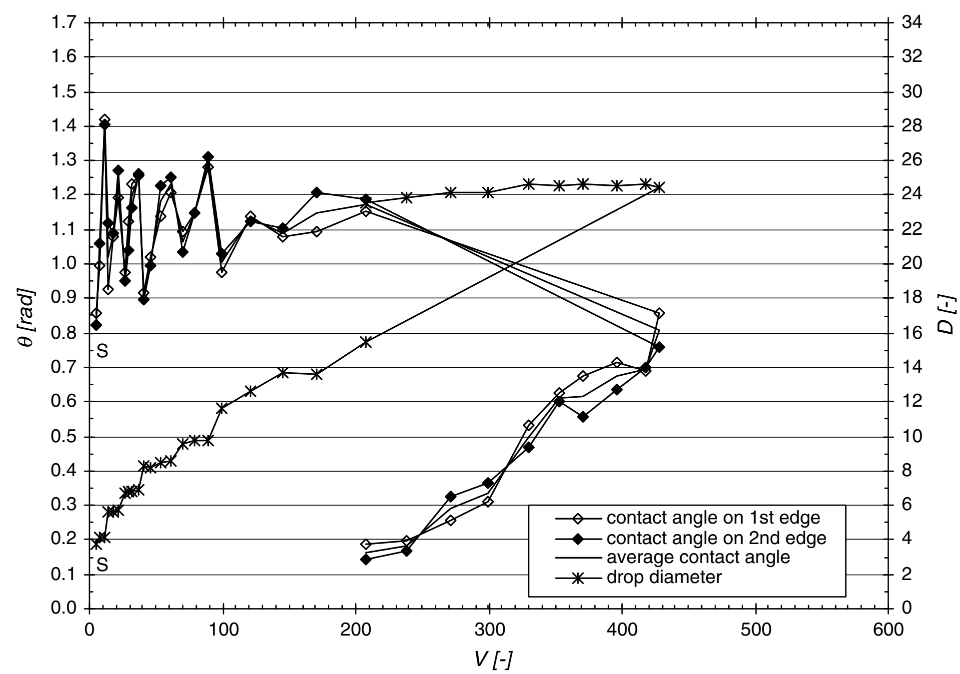

Fig. 5. Contact angle on both edges and diameter of the drop on copper with roughness $R_z = 11$ μm.

the diameter increased a bit when the water was dropping. It could be caused either by a measurement error or by a flow of a drop before the next photography was shot. It means that a drop might have changed to a more stable state of equilibrium or to unsymmetrical shape.

As we can see copper is the most wettability material among the presented materials and it is hydrophilic. Stainless steel has the least wetting properties (see Figs. 11 and 12), next are brass (see Figs. 6 and 7) and aluminium (see Figs. 8–10) which are wetted slightly better. If we compare Fig. 5 and Fig. 9 it could be seemed that copper is only a bit better wetted material than aluminium. However, it must be noticed that the largest drop had a volume 428 on copper and 547 on aluminium before the volume of a drop was started to decrease.

The differences in wettability of tested material can be explained by the existence and behaviour of a microfilm layer. If any copper surface is wetted, the molecules of

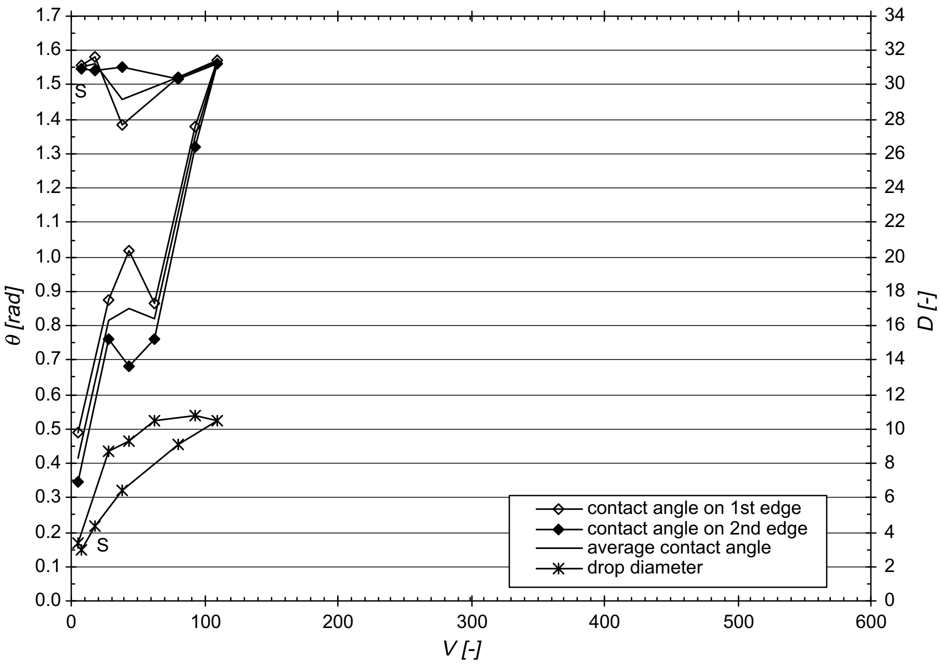

Fig. 6. Contact angle on both edges and diameter of the drop on brass with roughness $R_z = 2.8$ μm and $R_a = 0.4$ μm.

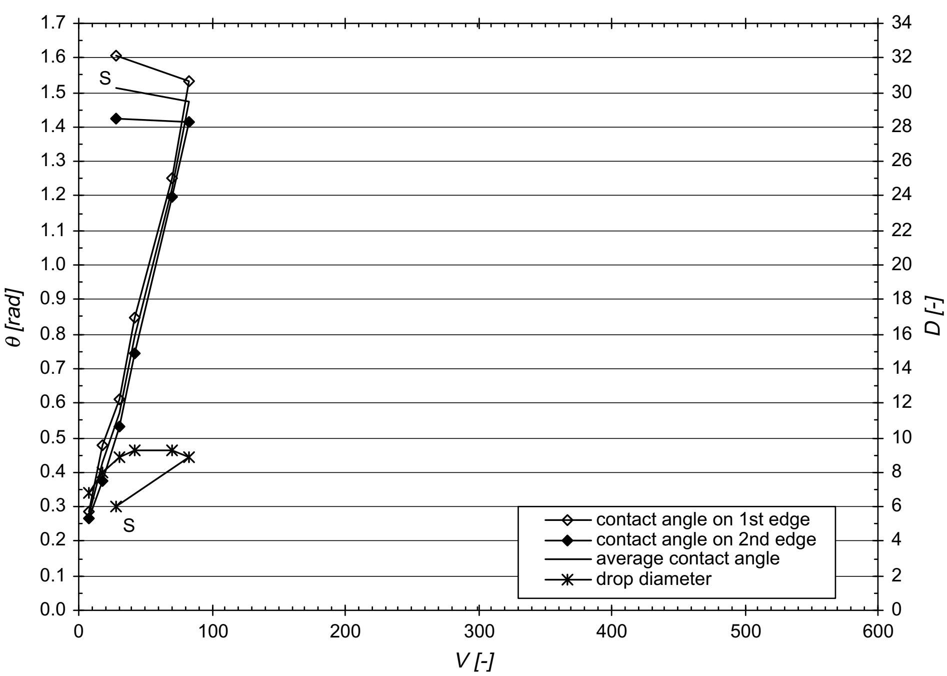

Fig. 7. Contact angle on both edges and diameter of the drop on brass with roughness $R_z = 17$ μm and $R_a = 3.5$ μm.

water will be adsorbed on it. When the water is moved from the wetted area, the tin adsorbed water layer retains on copper surface. As a result, the wetted area does not shrink, but the contact angle decreases.

The weaker wetting properties of aluminium, brass and stainless steel can be explained by the process of passivation, e.g. covering with the thin layer of the oxide. The zinc, aluminium or chromium oxides are hydrophobic. The passivation of copper is not such a quick process as it is in case of aluminium, zinc (brass consists of copper and zinc) or chromium (which is a compound of stainless steel), so the surface of copper plate remains hydrophilic.

A different situation is observed when the water is dropping. The drop on copper and aluminium and stainless steel tends to keep the wetted area. The disparate behaviour is observed in the case of brass. The drop shrinks immediately. This process can be delayed only by the roughness when decreasing of volume got started. It can

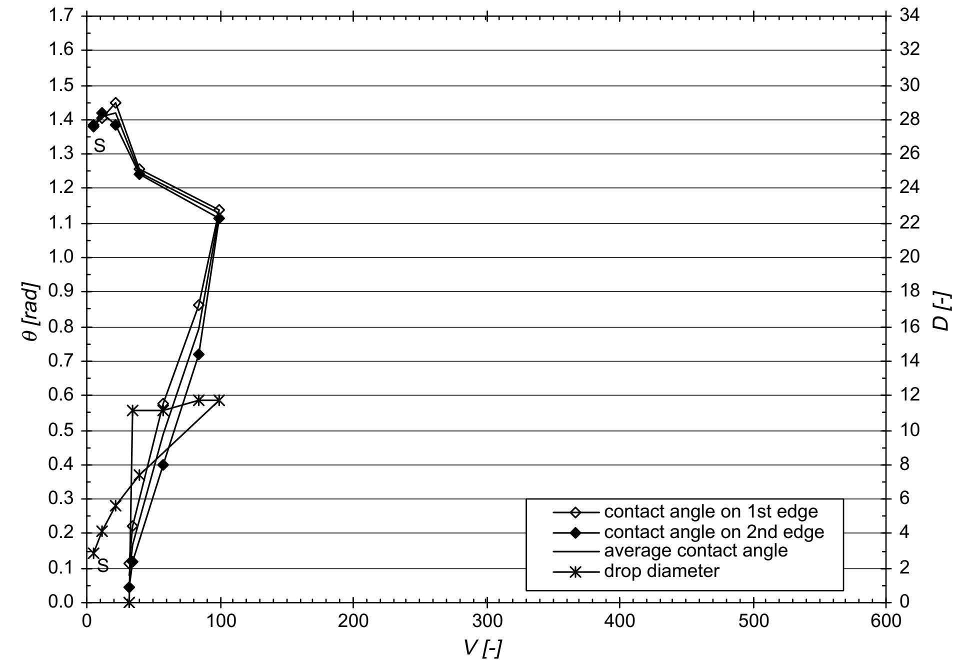

Fig. 8. Contact angle on both edges and diameter of the drop on aluminium with roughness $R_z = 7$ μm and $R_a = 1.3$ μm.

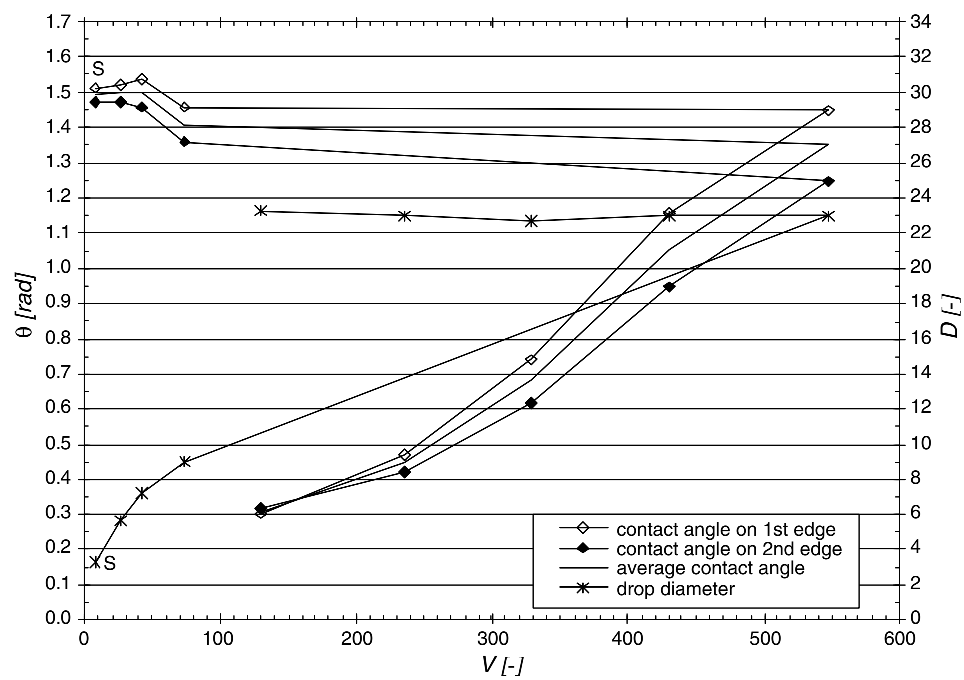

Fig. 9. Contact angle on both edges and diameter of the drop on aluminium with roughness $R_z = 7$ μm and $R_a = 1.3$ μm.

be said that aluminium and stainless steel change their properties and stay a lot more hydrophilic. It is very interesting situation which, has not been observed so far.

The disparate properties of aluminium, stainless steel and brass could be explained by a crystal structure. Aluminium oxide is described by the chemical formula Al_2O_3 and has a hexagonal close packed coordination geometry. Aluminium possesses a face centred cubic crystal structure. In order to form a molecule of aluminium oxide, two atoms of aluminium and three atoms of oxygen must take part, so a change to lattice structure proper for the aluminium oxide is needed. Otherwise it is not any state of force equilibrium among the atoms of aluminium and oxygen. Because no change in crystal structure of aluminium was noticed, there are unbalanced forces which are weaker than in a metal surface layer without any oxide layer. The similar situation can be observed in the case of stainless steel, but the non-reactive surface film makes up chromium oxide

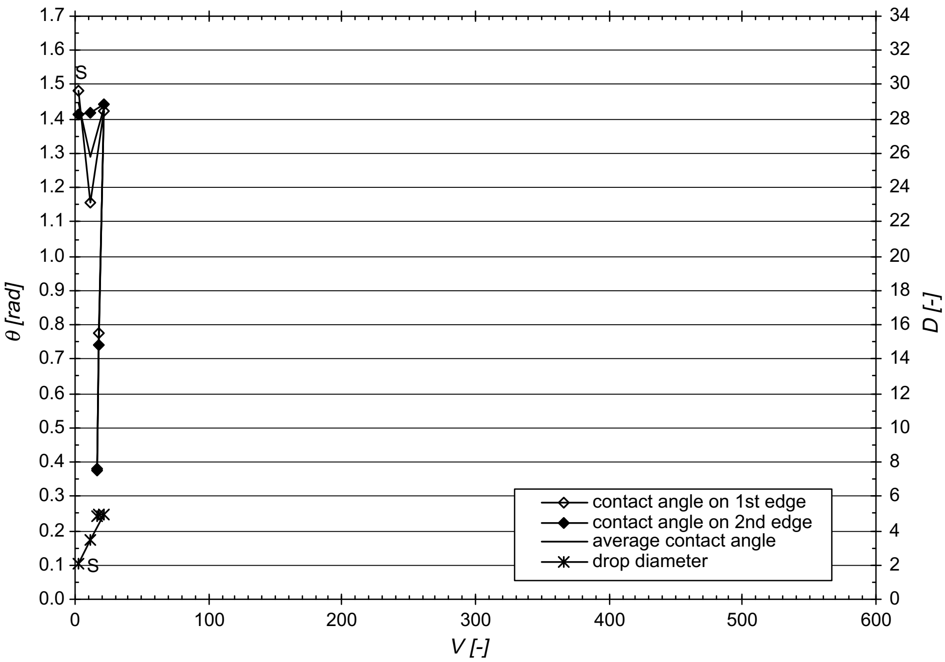

Fig. 10. Contact angle on both edges and diameter of the drop on aluminium with roughness $R_z = 25$ μm.

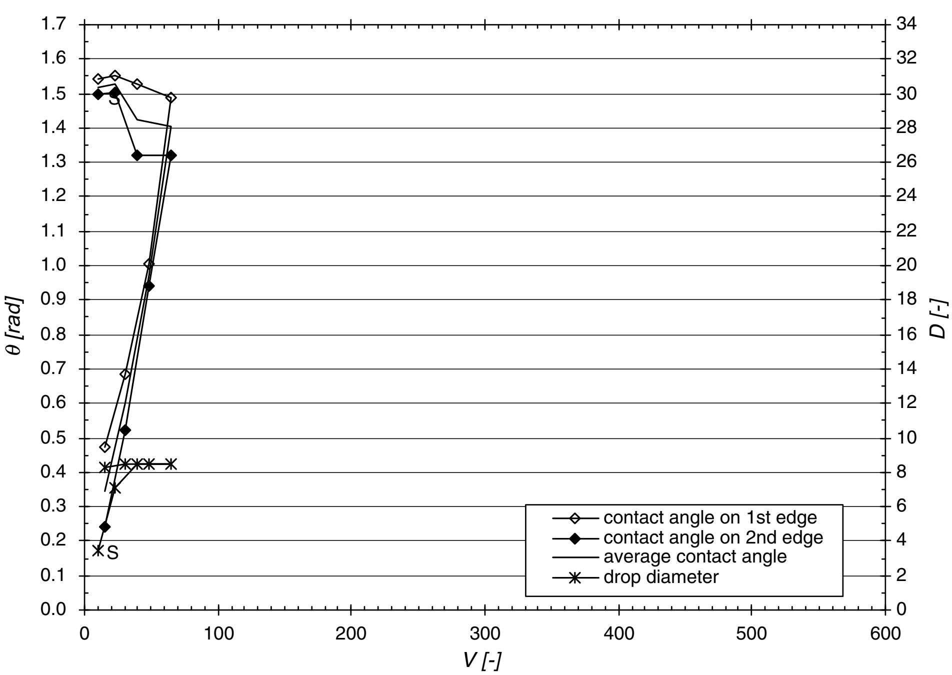

Fig. 11. Contact angle on both edges and diameter of the drop on stainless steel with roughness $R_z = 0.8$ μm and $R_a = 0.12$ μm.

Cr_2O_3. Chromium atoms are displaced among atoms of other chemical elements in steel. Like in above case, the interaction among atoms in a molecule of chromium oxide must be unbalanced. If a barrier of hydrophobic aluminium oxide or chromium oxide has been overcome, e.g. water has wetted the surface, the molecules of water can be adsorbed on the metal surface. As a result, water is not taken out from the wetted area when a drop has been started to decrease. Zinc in brass is arranged sparsely. One zinc and one oxygen atoms form a molecule of zinc oxide, so they can form a balanced molecule. Therefore, no unbalanced forces attractive to the water molecules exist and brass retains his hydrophobic properties. Needless to say that it is only a hypothetic explanation.

2.3.1. The impact of roughness

The higher roughness has no effect on copper surface, it changes neither the drop's diameter nor contact angle

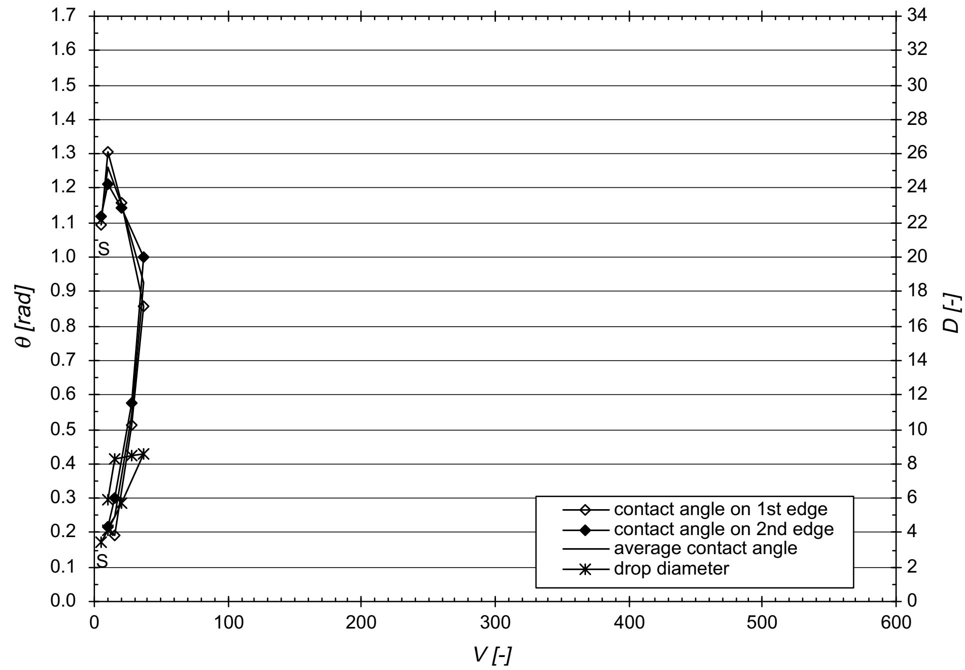

Fig. 12. Contact angle on both edges and diameter of the drop on stainless steel with roughness $R_z = 5$ μm and $R_a = 1.2$ μm.

to volume 30. For bigger drops, it increases the contact angle and makes diameter smaller. In the case of aluminium the lack of the impact of roughness on magnitude of diameter and contact angle was observed. There was no influence of higher roughness during enlargement of the drops on brass surface and during decreasing to 30. When a drop became smaller its diameter was wider and contact angler was smaller. The interesting behaviour of a drop on stainless steel surface was observed. When volume of the drop is less than 15 higher roughness makes contact angle smaller but diameter longer. It seems strange but it could be explained that higher roughness counteracts make drop narrower.

The roughness can distort the horizontal layout measurement, see in Fig. 13. If a geodesic level is placed along line AB, the horizontal level will be different from the one indicated by CD line. Such situation might have contributed to differences between contact angles on two drop edges (cf. Fig. 9). However, if the bigger values are on the one edge and then on the second, the reason for differences is roughness or surface heterogeneity, e.g., Fig. 5.

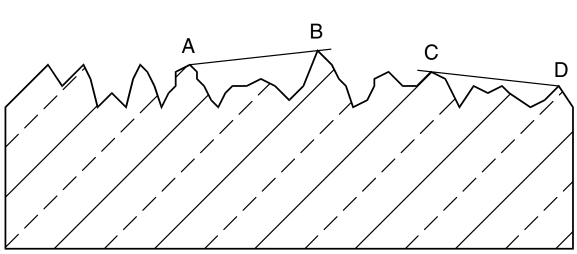

Fig. 13. The solid surface with magnified roughness.

3. Conclusions

- For drops whose volume is lower than 40, the drop diameters are similar and they are not depended on material components or roughness.
- Copper has the best wettability properties, next are: aluminium, brass and stainless steel.
- During the volume decreasing water on copper, aluminium and stainless steal a drop tends to keep up the wetted area, but one on brass has a tendency to decrease the wetted area.
- The existence of the critical contact angle value was recognised. Beyond its value a drop widens and contact angle decreases significantly.
- The critical contact angle value depends on chemical properties of surface and surface roughness.
- It is necessary to measure the contact angle on both edges of a drop.

Acknowledgements

I wish to thank Prof. M. Trela for his help in experiments.

This scientific research was financed by Bialystok Technical University as Dean's Project S/WBIS/23/08.

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