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Wetting characteristics of copper on niobium

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Sessile drop experiments have been performed in a temperature range between 1090 and 1300° C, aiming to study the wetting of niobium by liquid copper and the influence of different atmospheres (argon, hydrogen, vacuum), crystallographic orientation, roughness, and oxygen doping of niobium on the wetting angle. At the peritectic temperature in the Cu–Nb system (1090° C) the contact angle is high, $\theta = 67°$, denoting poor wetting. With increasing temperature, θ decreases steadily for all samples. The wetting is at its lowest for the oxygen-doped samples and at its best for samples annealed under a hydrogen atmosphere. A new mechanism is suggested and discussed for oxygen degassing of niobium through liquid copper.

1. Introduction

The wetting between a liquid and a flat solid surface is usually characterized by the contact angle θ [1], which is related to the surface tensions γ_{sv}, γ_{sl}, γ_{lv} (sv: solid–vapour, sl: solid–liquid, lv: liquid–vapour interfaces) (Fig. 1) by the well-known Young equation [2, 3]

$$\gamma_{sv} = \gamma_{sl} + \gamma_{lv} \cos\theta \qquad (1)$$

In principle any change of the interfacial characteristics should produce variations of the surface tensions, and hence of θ. Thus it is possible that a small amount of additives in the liquid, or the effect of some special atmosphere, is able to improve the wettability by lowering θ.

Our interest in studying the wetting between niobium and copper originates from the effort to clarify a new method of preparation of Cu–Nb_3Sn superconducting wires [4]. This new method is based on the liquid-phase sintering approach to produce perfectly dense samples containing 30 wt % Nb, having good mechanical properties. It is well known that with good wetting the liquid infiltrates into the voids between the solid particles and promotes densification [5].

Despite the increasing interest in the Cu–Nb alloy because of new technologies for superconducting wire fabrication [6], from the metallurgical point of view there remains a broad lack of basic information about this system. With respect to wetting and surface tension calculations, only limited information is available for 1500° C [7]. In the present paper the wetting behaviour in the temperature range between 1090 and 1300° C was investigated by means of several sessile drop experiments. Previous experiments have shown that in this temperature range densification during liquid-phase sintering is at its best.

2. Experimental procedure

The samples used in this work (Table I) were prepared using a pure niobium sheet (99.9%, with 740 wt ppm Ta) of 1 mm thickness, and a high-purity copper wire (99.999%) of 1.5 mm diameter. Each niobium plate was cut with dimensions typically $10 \times 15\,mm^2$. Except for Sample SD–9, all plates were polished to guarantee a flat and smooth surface. Sample SD–9 was ground with emery paper (SiC, No. 500, pressure $20\,g\,cm^{-2}$) to study the effect of roughness on wetting.

Fig. 1 shows a schematic drawing of the experimental set-up for the sessile drop experiments. The sample, consisting of a niobium plate with a small cylinder of copper (25 to 30 mg) on top,

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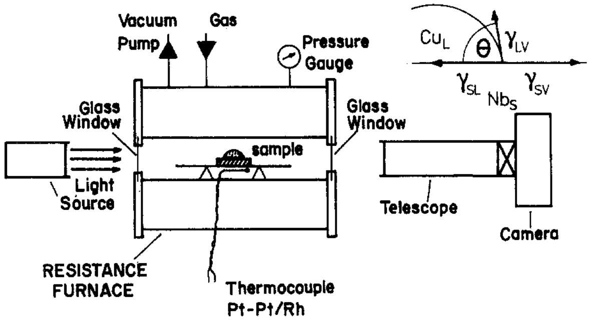

Figure 1 Schematic drawing of the experimental set-up for sessile drop experiments.

is located in the central region of the resistance furnace, between the light source and a photographic camera. This arrangement permits photography of the silhouette of the sample at any stage of the experiment.

A time interval of 5 min was enough for the copper droplet to reach its equilibrium configuration at each fixed temperature for all samples, except those under an H_2 atmosphere. In this case annealing periods of 25 min were required. The temperature was automatically regulated by a Eurotherm Controller using a Pt–Pt/Rh thermocouple, with an accuracy of ± 7° C. All optical parts were adjusted in order to minimize interference effects, which cause fringes around the base of the droplet [8].

The wetting characteristics were determined by taking photographs of the samples at each temperature given in Table I, and a subsequent evaluation of the negative film with respect to the contact angle and shape. All θ values represent an average between the two angles observed in the left and right sides of the silhouette. In general, the difference between these two angles was small. An error of $\pm 2°$ was estimated for θ, which is particularly relevant for $\theta < 20°$. Table I and Fig. 2 summarize the results and the characteristics of the samples. Table I shows values of θ for temperature $T = 1090$, 1100, 1200 and 1300° C; however, almost all samples were also measured at $T = 1150$ and 1250° C, as shown in Fig. 2.

3. Results and discussion

The Cu–Nb phase diagram [9, 10] shows no intermetallic phases in the whole composition range. The solubility at ambient temperatures (20° C) is very small for niobium in copper (< 0.2 wt %) and negligible for copper in niobium [11]. A peritectic reaction exists at 1090° C, where the maximum solubility of copper in niobium is 1.4 wt % [10] and of niobium in copper is 1.6 wt % [9]. The literature shows some variation in these values, as well as in the equilibrium phase diagram. Meanwhile, there is no doubt about the very small mutual solubility around the peritectic temperature.

In the case of binary systems A–B having very low mutual solubilities it has been shown [12], using the monolayer model for calculating the surface tension terms γ_{sl}, γ_{sv}, and γ_{lv}, that the equilibrium contact angle at the melting point of metal B is given by the equation

$$(1 - \cos\theta) = K(T_{\mathrm{f}}^{\mathrm{A}}/T_{\mathrm{f}}^{\mathrm{B}} - 1) \qquad (2)$$

where $T_{\mathrm{f}}^{\mathrm{A}}$ is the melting point of the substrate A, $T_{\mathrm{f}}^{\mathrm{B}}$ the melting point of the liquid droplet of metal B, and K is a constant equal to 0.28 as calculated by Eustathopoulos and Pique [12].

TABLE I Characteristics and contact angles for sessile-drop samples of Cu–Nb (for experimental details see text)

Samples		Contact angle θ (deg)			
No.	Niobium characteristics and treatment	$T = 1090°$ C	1100° C	1200° C	1300° C
SD–1	Polycrystal, H_2 atmosphere, 870 mbar	68	65	14	–
SD–2	Polycrystal, vacuum, 1.5×10^{-6} mbar	65	60	35	15
SD–3	Polycrystal, argon atmosphere, 870 mbar	69	66	42	17
SD–4	Polycrystal doped with 6.5 at % O, vacuum	85	85	79	59
SD–5	Single crystal (1 0 0), vacuum	64	64	43	34
SD–8	Polycrystal doped with 1.5 at % O, vacuum	65	64	56	19
SD–9	Polycrystal, rough surface, vacuum	76	76	51	12
SD–10	Single crystal (1 1 0), vacuum	74	74	44	9
SD–11	Polycrystal, H_2 atmosphere, 870 mbar	38	–	8	0

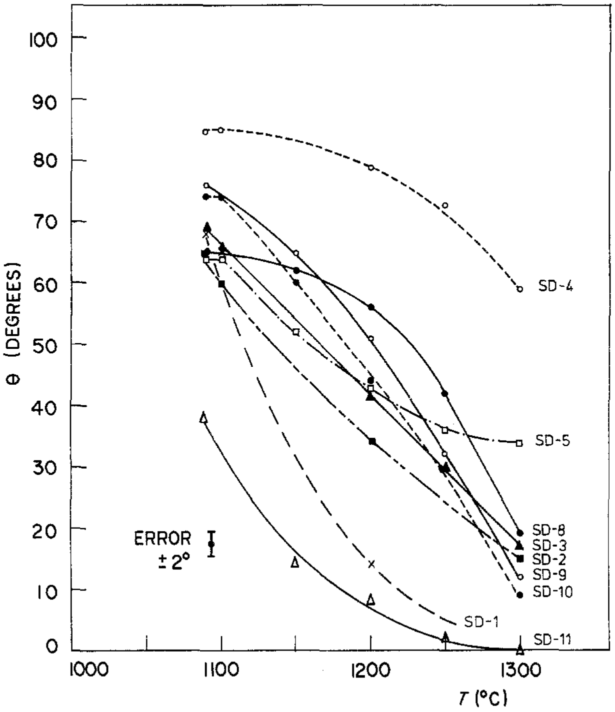

Figure 2 Plot of contact angle θ against temperature, T. The label on each curve refers to Table I.

The data for the Cu–Nb system are displayed in a plot of $(1 - \cos\theta_{\text{exp}})$ against T_f^A/T_f^B where θ_{exp} is the measured value (Fig. 3), together with data for other immiscible binary alloys. In our experiments an average value of $\theta_{\text{exp}} = 67°$ for all polycrystalline samples at 1090° C was found. The dot–dashed line in Fig. 3 was computed including the new Nb–Cu results. These experimental results are represented by

$$(1 - \cos\theta_{\text{exp}}) = 0.34(T_f^A/T_f^B - 1) + 0.05. \tag{3}$$

Within a reasonable experimental scatter the data of the Cu–Nb system measured in this work fit with the other data. The constant was determined, including Cu–Nb data, as 0.34. This value is closer to the predicted value of 0.28 than the value 0.36 measured by Eustathopaulos and Pique [12].

The value of $\theta_{\text{exp}} = 67°$ at 1090° C means a bad wetting between niobium and copper. However, as will be seen below, θ may vary depending on different factors, and may even attain perfect wetting ($\theta = 0°$).

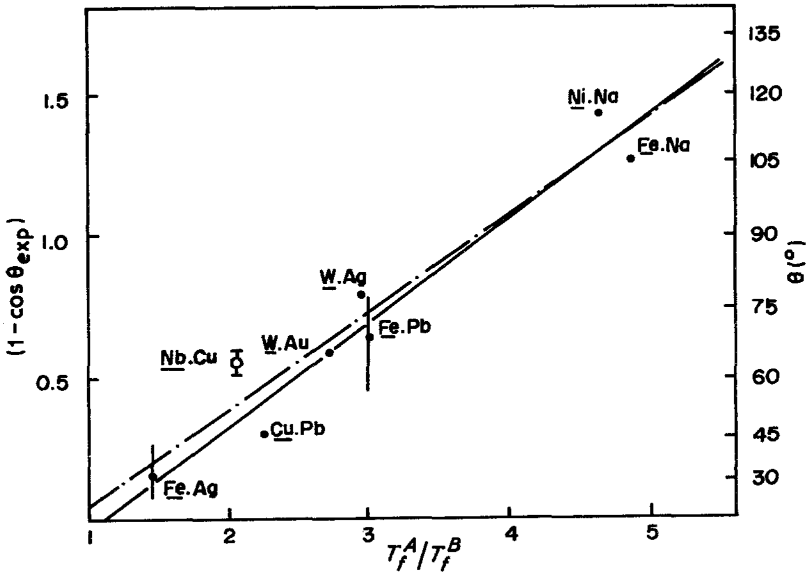

Figure 3 Experimental verification of Equation 2 (see text). The continuous straight line was computed in [12] without the Nb–Cu point. The dot-dashed line was computed in this work including the Nb–Cu point.

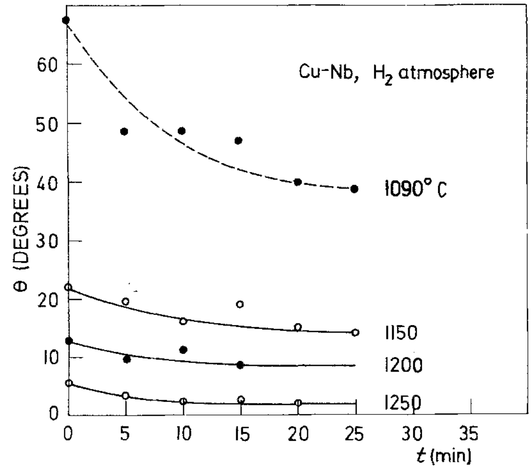

Figure 4 Spreading of liquid copper on a plate of niobium polycrystal under H$_2$ atmosphere, as a function of time t at different temperatures.

3.1. Effect of atmosphere and time

The sessile drop experiments performed in an H$_2$ atmosphere clearly show an improved wetting between solid niobium and liquid copper. This follows from experiments on samples SD–1 and SD–11. SD–1, however, shows higher θ values than SD–11 for a given temperature. This is due to differing annealing periods at a given temperature. In the case of annealing under argon (purity 99.997%) or under vacuum, each temperature was held constant for 5 min only, which was found to be sufficiently long. Under H$_2$ (purity 99.999%), however, this time interval was not long enough for the copper droplet to attain its equilibrium shape. Under H$_2$ atmosphere it needed 20 min to reach the equilibrium angle (Fig. 4).

The very different behaviour of wetting either in H$_2$ or in other atmospheres (argon, vacuum) may be related to the preferential reduction of oxygen dissolved in niobium by hydrogen, through liquid copper. Deoxidation of niobium below 1600° C is normally performed by annealing the oxygen-containing samples in a reducing atmosphere, preferentially in hydrocarbons due to the favourable conditions for the formation of CO. In this temperature range the reduction of O$_2$ content using H$_2$ as a reducing agent is possible from thermodynamic data [13] if the H$_2$O partial pressure is kept very low ($p_{H_2O} \ll 10^{-6}\, p_{H_2}$). These conditions are difficult to establish even with high-purity H$_2$ and using ultra-high vacuum equipment. In our experiments H$_2$ gas was used with 10 vol ppm residual H$_2$O content. For 1100° C and an H$_2$ atmosphere at 870 mbar (1 mbar = 10^{-2} Pa) the minimum concentration of oxygen in niobium is calculated as about 3000 wt ppm.

Under the given conditions a reduction of the oxygen concentration should not be possible. We found that the Vickers hardness of the niobium samples, which mainly results from solid-solution hardening by oxygen, is considerably reduced underneath the copper droplet (HV 0.025 = 95), whereas it keeps at higher levels (HV 0.025 = 130) in the copper-free regions. It is therefore assumed that the oxygen content may be reduced in this region of the sample because of kinetic reasons, i.e. through an increased reaction rate at the Nb–Cu or Cu–gas interface compared with a direct oxygen degassing from niobium with H$_2$, and by small oxygen activities at the Nb–Cu boundary caused by a reduced rate of the back reaction according to

$$[O]_{\text{Cu or Nb}} + H_2 \rightleftharpoons H_2O$$

The back reaction may be reduced by evaporating copper atoms which collide with H$_2$O molecules. Further experiments aiming to demonstrate and explain these mechanisms are still under way and will be published elsewhere. The experiments under vacuum (SD–2) and under argon (SD–3) gave similar results (Fig. 2). It seems that the inert gas atmosphere has nearly the same effect as a vacuum (1.5 x 10^{-6} mbar) on the superficial tensions γ_{lv} and γ_{sv}.

3.2. Effect of crystallographic orientation

An effect of the crystallographic orientation of the niobium substrate on θ can be expected because the surface tension terms γ_{sv} and γ_{sl} are related to the collective atomic interactions, which depends on the density of atomic packing in the solid surface [14].

The single-crystalline samples SD–5 and SD–10, with surface planes (100) and (110) respectively, show different θ against T curves (Fig. 2). The difference is more pronounced for higher temperatures, reaching $\Delta\theta = 25°$ at $T = 1300°$ C. The more densely packed plane (110) shows a better wettability for $T > 1200°$ C than the less densely packed plane (100). However, below 1200° C this result is inverted, although the differences $\Delta\theta$ for the same T are smaller. In addition a receding angle effect was observed for Sample SD–10, with a variation of $\Delta\theta = 6°$ between $T = 1300°$ C and $T < 1090°$ C during cooling of the sample (cooling rate ~ 50 deg

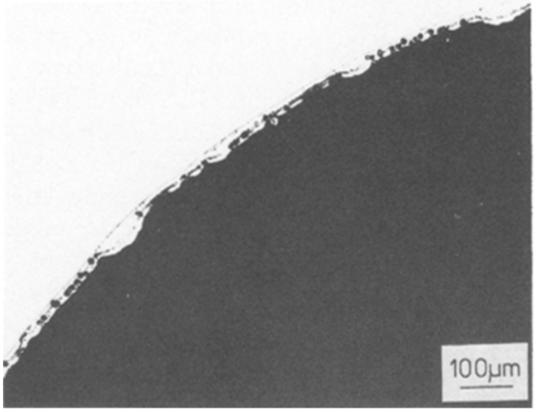

Figure 5 Detail of the copper droplet contour on the niobium single-crystal Sample SD–5, showing a small receding effect.

min^{-1}). This receding effect was also observed for SD–5, as shown by the drop contour in Fig.5, but on a very small scale, insufficient to produce any detectable changes in θ during cooling. For polycrystalline samples the receding effect was imperceptible.

The dependence of θ on crystallographic orientation should produce an irregular contour (on a grain-sized scale) for the advancing copper droplet on a polycrystalline sample. In fact, Sample SD–2 (Figs. 6 and 7) shows this effect. It seems that the wetting of some grains is low, while other orientations are favouring this process. The copper droplet spreads preferentially along grain boundaries. However, on a coarse scale the contour of the copper droplet shows a generally circular shape. It can be stated that for a fine grain structure the average values γ_{sl}, γ_{sv} and thus θ tend to be isotropic.

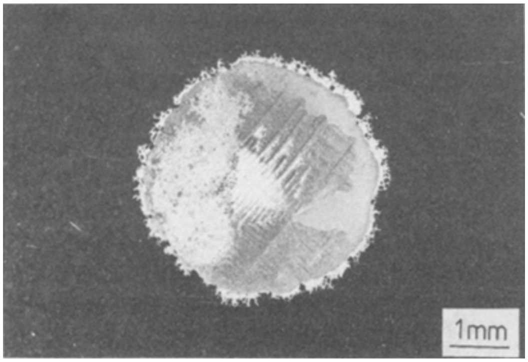

Figure 6 Top view of the copper droplet on a niobium polycrystal in Sample SD–2 (under vacuum), showing the irregular contour and spreading along the grain boundaries.

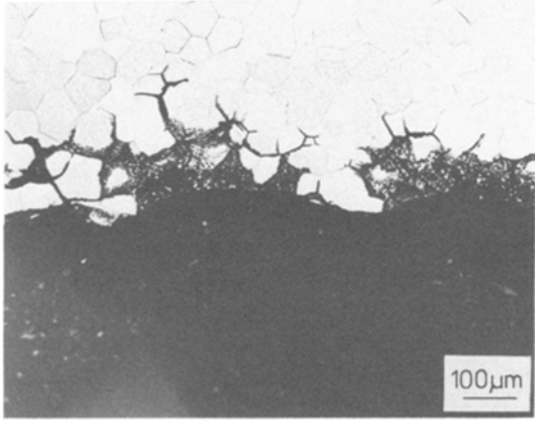

Figure 7 Detail of copper spreading along the niobium grain boundaries in Sample SD–2.

3.3. Effect of roughness

The θ values for the sample having a rough surface (SD–9, Fig. 2) are higher than those for the polished polycrystalline samples up to $T \sim 1250^\circ$ C. This result contradicts the relation proposed by Wenzel [15], that predicts a lower apparent contact angle θ' (experimentally determined) with respect to the intrinsic angle θ found for a smooth surface. The relation is:

$$\cos\theta'/\cos\theta = r \qquad (4)$$

where the ratio between the true area A and the apparent (or geometric) area A' is the roughness factor $r = A/A'$. The value of r was estimated to be 1.6 for SD–9, which is relatively high. Probably the action of surface asperities as energy barriers can be explained our present result. These energy barriers separate positions of metastable equilibrium for the drop contour [16]. The advancing contact angle during spreading can then be higher than the equilibrium value according to Wenzel's relation [17]. This is in agreement with Bailey and Watkins [18] who found a hysteresis of the contact angle between spreading and receeding of a liquid on some rough solid surfaces.

3.4. Effect of oxygen

The negative effect of oxygen on the wetting between solid niobium and liquid copper is shown in Fig. 2 by the oxygen-doped samples SD–4 (6.5 at% O) and SD–8 (1.5 at% O). Even for $T = 1300^\circ$ C the contact angle is high, e.g. $\theta = 59^\circ$ for SD–4 and 19° for SD–8. For the sample doped with 6.5 at% O a thin layer of NbO was detected on the surface by X-ray diffractometry. This sample

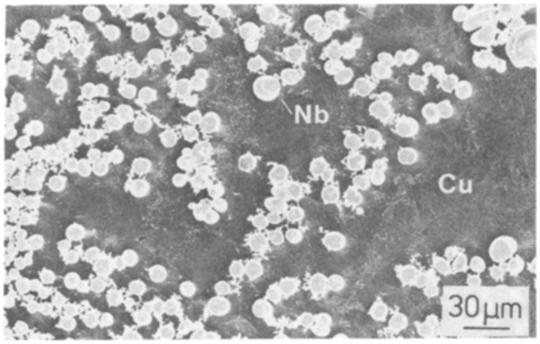

Figure 8 Niobium precipitates on the surface of the copper droplet in Sample SD–3 (under argon).

confirms the general rule that wettability is low for refractory oxides [5].

3.5. Wetting mechanisms

All niobium samples were slightly attacked by the liquid copper at higher temperatures. Niobium is dissolved into the liquid copper, probably helping to lower the surface tensions γ_{sl} and/or γ_{lv}, and thus the contact angle.

The surface of the copper droplet for Samples SD–1, SD–3 and SD–11 that were submitted to a higher cooling rate ($\sim 140^\circ \mathrm{C\,min^{-1}}$), shows a regular distribution of niobium precipitates. From the top-view picture (Fig. 8), and also from cross-sectional pictures, we found an average size of $20\,\mu$m for the niobium precipitates in Sample SD–3. During cooling the solubility of niobium decreases in liquid copper, producing the niobium precipitates. The size of the precipitates depends on the cooling rate [19]. The niobium precipitates are enriched at the surface because of their lower density.

Diffusion of copper along the niobium grain boundaries seems to be an important mechanism for spreading and for fixing the droplet contour by a kind of "anchoring effect" (see Figs. 6 and 7). Using microprobe analysis we found up to 3.5 wt% Cu in the grain boundaries of the niobium plate, in a distance of 10 to $20\,\mu$m in vertical direction from the Cu–Nb interface. Within the grains of the niobium plate the copper concentration in the vicinity of the Cu–Nb boundary was lower than 1 wt%, as expected [11]. The major dissolution of the niobium plate also took place along the grain boundaries.

At first sight it was thought that scratches on the surface of the niobium plate could produce the same effect as grain boundaries. To test this hypothesis we prepared Sample SD–9 by grinding its surface, using emery paper with an average particle size of $18\,\mu$m. However, spreading of liquid copper along these scratches was much lower than along grain boundaries. This fact is explained by the higher energy state of grain boundaries compared to mechanically produced scratches. Dissolution along the grain boundaries should be promoted because of this minimization of the free energy.

4. Conclusions

1. The wetting of niobium by liquid copper is low at the peritectic temperature $T = 1090^\circ$ C. The average contact angle for polycrystalline niobium substrates was determined as $\theta = 67^\circ$. At this temperature the metals are practically immiscible. The results were therefore tested against the Eustathopoulos equation (Equation 2 of [12]), derived for a monolayer model to calculate the surface tension for two immiscible phases. As shown in Fig. 3 and Equation 3, a reasonably good agreement between experimental and theoretical prediction was found.

2. With increasing temperature the contact angle decreases steadily for all samples (Fig. 2). The dissolution of niobium into the liquid copper, which helps to lower the surface tensions (γ_{sl} and/or γ_{lv}), is the most relevant effect being activated by temperature. Copper diffusion along the niobium grain boundaries seems also to be an important mechanism for spreading and anchoring the droplet contour.

3. High contact angles were found in the case of oxygen-doped samples SD–4 (6.5 at% O) and SD–8 (1.5 at% O). Wetting improves for samples treated under H_2 atmosphere (SD–1 and SD–11) up to perfect wetting ($\theta = 0^\circ$). The presence of liquid copper may increase the deoxidation rate of niobium by H_2, or decrease the oxygen activity at the Nb–Cu interface. Decreased values of the microhardness of niobium below the copper droplet corroborate this idea.

4. The effect of crystallographic orientation was verified in two samples of single-crystalline niobium with the surface parallel to the (100) and (110) planes. For the polycrystalline samples, an irregular contour for the copper droplet was revealed on a grain-sized scale (Figs. 6 and 7).

5. The effect of roughness was analysed using a sample with Wenzel's roughness factor $r \sim 1.6$ (Equation 4). Wetting was lower for rough surfaces, contrary to the prediction of Wenzel's equation.

The action of energy barriers due to the excessively coarse surface can perhaps explain this result.

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