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ANTIFOULING AND ANTICORROSION PROPERTIES ON SURFACES OF TiO₂ NANOMETER FILMS COATED WITH LIQUID PHASE DEPOSITION

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ABSTRACT

Fouling on heat transfer surface is an intractable problem in industrial heat exchangers and several techniques have been suggested to inhibit scale deposition on surfaces. Surface coating is one of such methods which can decrease the surface free energy and thus reduces the adhesion force between scale and surface. In this paper, liquid phase deposition technique was applied to coat titanium dioxide (Vs. TiO₂) thin films on red copper substrates with film layer thickness in nanometer order. Coating thickness, contact angle and topography were measured with x-ray diffraction (Vs. XRD), contact angle analyzer and scanning electron microscopy (Vs. SEM), respectively. Surface free energy of coating layers was calculated based on the contact angle. It is around 20 mJ·m⁻ ² for layer thickness less than 100 nm. Heat transfer and fouling characters in pool boiling of distilled water and calcium carbonate (Vs. CaCO₃) solution on coated surfaces were investigated experimentally. Heat transfer enhancement was observed on coated surfaces compared to untreated or polished surfaces. Coated surfaces with thickness in nanometer order extend the fouling induction time by about 4~9 times longer than untreated surfaces. There may be an optimum range of coating thickness and microstructure for heat transfer enhancement and fouling prevention. Corrosion resistance behavior of coated surfaces under extreme environments of acid, alkali and salt solutions at room temperature was also explored qualitatively by soaking the coated samples into the corrosive media including sodium chloride, hydrochloric acid and sodium hydroxide solutions a few hours with the concentrations of 25%, 30% and 30%, respectively. The results indicate that coated surfaces can resist corrosion in alkali solution when soaked in 200 hours. However, it was eroded in the acidic solution after 100 hours. In salt solution, it was eroded until after 600 hours. The present work may open a new nanometer coating route to inhibit fouling deposition and corrosion on heat transfer surfaces in industry evaporators, which is very important for energy saving in the process industries.

INTRODUCTION

Fouling accumulation on heat transfer surfaces in heat exchangers, especially on boiling surfaces in industry

evaporators, is a troublesome problem because it can lead to a drastic increase of heat resistance and therefore result in a decreased heat-transfer efficiency of heat exchangers (Branch and Müller-Steinhagen, 1991; Steinhagen, et al.,1993; Müller-Steinhagen and Zhao,1997; Yang, et al.,2004; Müller-Steinhagen, et al.,2005; Liu, et al., 2007; Herz, et al., 2008; Bansal, et al.,2008).

Several approaches towards reduction of fouling adhesion or occurrence on heat transfer surfaces have been suggested in the past years. One of the most potential techniques is to lower the surface free energy by surface engineering methods. The reason is that on a surface with high surface free energy, excess adsorption force exists and fouling is easy to adhere (Müller-Steinhagen and Zhao, 1997; Foerster et al., 1999; Liu, et al., 2007).

There are four types of surface engineering routes (Liu, et al., 2007a). First one is named surface coating characterized with a certain thickness of film layer on the surface to be modified, such as electroplating, chemical plating, physical vapor deposition (sputtering and vacuum evaporation etc.), chemical vapor deposition and sol-gel. Second one is called surface modification by which only chemical compositions of the surfaces are changed and there is not obvious thickness of film layer on the surfaces, such as ion implantation. The third one is called surface treatment by which the texture structure and stress of the surfaces are altered without additional film layer and variation of chemical compositions, such as blasting shot and quenching. The fourth one is the combination of the above three types. Sometimes, all of them are called surface modification (Santos, et al., 2004).

The most recent crucial work about fouling inhibition on heat transfer surfaces in heat exchangers by surface modification techniques including ion implantation, sputtering, plasma arc deposition, plasma enhanced chemical vapor deposition, autocatalysis and sol-gel methods was done by Müller-Steinhagen and his multinational research group (Santos, et al., 2004; Rosmaninho, et al.,2007;2008a;2008b;). The modified surfaces were characterized with different surface analysis instruments. Fouling experimental results in convective, pool or flow boiling system with typical fouling solutions including simulated milk ultrafiltrate demonstrate that lowenergy surfaces, such as the surface with Ni-P-PTFE material layer can significantly reduce the fouling deposition compared to untreated or polished surfaces.

In spite of these great efforts, a desired modification technique that can meet the demands of industry applications such as process simple, inexpensive and easy to scale-up still lacks. A surface coating technique called liquid phase deposition (LPD) may be such a method.

It was introduced into antifouling investigations (Liu, et al., 2007b). Fouling inhibition and boiling enhancement on TiO_2 film surfaces coated by LPD with thickness in micrometer order on inner wall of heating tube under flow boiling of CaCO₃ solution were observed. TiO_2 being chosen as a coating material is due to its unique characters and potential applications in energy conservation.

TiO₂-coated surfaces exhibit super-hydrophilicity when exposing it to an ultraviolet ray. TiO₂-coated surfaces with film thickness in micrometer order prepared by dipping, sputtering or plasma-irradiating process can enhance pool boiling, immersion cooling, falling film evaporation and single water drop evaporation under radiation of ultraviolet ray (Takata, et al., 2003; 2005). However, on a super-hydrophobic surface coated with fine particles of nickel and PTFE by means of electrolytic plating with contact angle to water of 152° in room temperature and thickness of 10×10^{-6} m, a stable film boiling occurs in very small superheating, and there is no nucleate boiling region. The vapor bubbles generated on the surface coalesce into a vapor film without departing from the surface (Takata, et al., 2006). Hence, the super-hydrophobic Ni-PTFE-coated surface seems not to be in favor of pool boiling heat transfer. On the other hand, the main reasons resulted in the self-cleaning functions of natural biosurfaces such as lotus leaves, rice leaves, cicada wings and water strider legs were contributed to their superhydrophobic natures and the micro- and nano-scale structures (Gao and Jiang, 2006). Therefore, the surface with middle hydrophobicty may be favorable both for boiling enhancement and fouling prevention.

Meanwhile, it is an interesting topic to investigate the fouling property on coated surface with thickness in nanometer order. The elementary results indicate that antifouling and flow boiling enhancement on TiO₂-coated surfaces may be improved further if the thickness of TiO₂ coating layer is in nanometer order (Liu, et al., 2007b). In order to explore the influence of coating layer thickness in nanometer scale on fouling and heat transfer properties, the coating method of vacuum evaporation was used to prepare TiO₂ film layers and fouling deposition in pool boiling of CaCO₃ solution was investigated (Wang, et al.,2007). The results indicate that all TiO₂ coating surfaces can inhibit $CaCO_3$ deposition, and the fouling induction time on TiO₂ coating surface in pool boiling with film thickness of 80nm is about 50 times longer than that of untreated or polished surface. However, the vacuum evaporation coating method is more expensive and more difficult to scale up compared to LPD method which is more attractive for industry applications.

Anticorrosion investigations on these coated surfaces are also meaningful because sometimes heat transfer fluids

are corrosive media. However, little work on such topic can be found. The goals of this work are to find good antifouling and anticorrosion TiO₂-coated surfaces. Section 1 presents the experimental description. This section includes preparation, characterization of test surfaces, pool boiling and corrosion experiments on test surfaces. Section 2 contains the experimental results and discussion. Section 3 is the concluding remarks.

1 EXPERIMENTAL

1.1 Preparation and Characterization of TiO₂-Coated Surfaces

1.1.1 Preparation of TiO₂-Coated Surfaces by LPD

The test substrates used in the present experiments are red copper plates. The size of test substrates for characterization is about 10mm×10mm×7mm, and that for heat transfer and fouling experiments is 110mm in diameter and 7mm in thickness. Three types of test surfaces were prepared: untreated, polished and coated surfaces.

Polished test samples were prepared from untreated substrates by finishing, polishing, oil removing, cleaning and drying. Finishing was carried out by using emery wheel with emery grits of Nos. 340 and 600. Polishing was performed by using polishing wheel with grinding pastes of emery sand particles in diameter of 1×10^{-6} m and 0.5×10^{-6} m. De-oiling was done by using 10% sodium hydroxide solution. Cleaning includes acetone ultrasonic cleaning and de-ionized water cleaning. Airing was carried out with natural air.

TiO₂ thin layers were coated on polished surfaces with LPD method. The polished samples after being dried were dipped into the homogeneous reaction solution in a reactor with liquid temperature control device. Deposition reactions began proper reaction conditions, including at concentrations of chemicals, temperature and reaction time etc. Test samples were treated in an electric muffle furnace (Type DRZ-4) including cleaning, drying and heat treating after deposition reaction finished. The temperature of heat treatment increased at a rate of 2°C per minute and then was kept in 150°C for one hour.

1.1.2 Characterization of TiO₂-Coated Surfaces

The topography of the test samples was measured with SEM (Philips, XL-30 type).

The coating thickness of the samples was determined by using high-angle XRD. XRD measurement was preformed with x-ray diffractiometer (Rigaku D/MAX 2200V/PC type). The thickness was calculated based on the diffraction information of substrate material copper (Cu).

The contact angles were measured by using both digital camera and JY-82 contact angle analyzer under room temperature. Distilled water and glycerin were used as test liquids. The contact angle on each test sample was measured at three times and the average was taken as the measured result.

The surface free energy was calculated on the measurement data of contact angles of coating surfaces according to GEO_{s} method (Michalski, et al., 1998).

1.2 Experiments on Pool Boiling and Fouling

The pool boiling experimental apparatus, flowchart, parameter measurements and calculations, fluid media and operation conditions are available in literature and only described here briefly (Wang, et al.,2007).

The experimental apparatus consists of a cylindrical stainless steel tank with inner diameter of 0.1m and height of 0.3m, a cylindrical copper heater with diameter of 0.08m and height of 0.06m wrapped with heating resistance wire and a glass condenser with heat-transfer area of $0.02m^2$.

The temperature measuring system consists of a few Pt resistance transducers, a signal amplifier, an A/D converter and an industrial computer 610. The temperatures along the center axis of the copper cylinder heater were measured by three Pt resistances embedded in the cylinder. Liquid temperature in boiling pool was also measured by Pt resistance.

Pool boiling of distilled water and $CaCO_3$ solution on different test surfaces was carried out. The operation was continuous for each test surface. The experiments were performed at atmospheric pressure. The data were recorded in an interval of 1800s. In each time for data recording, the data were sampled with a frequency of 10 Hz and time length of 10s. Heat flux and boiling surface temperature were determined by using three temperatures in the cylindrical heater and their axial locations according to onedimensional conduction theory. The heat resistance of coating layer is ignored during the surface temperature calculation because the coating thickness is in nanometer scale. Heat transfer coefficient of pool boiling was calculated based on the heat flux and heat-transfer temperature difference.

Calcium carbonate water solution was prepared by dissolving a certain amount of analytical grade $CaCl_2$ (0.0721kg·m⁻³) and NaHCO₃ (0.1092kg·m⁻³) in distilled water with temperature of 293K. The concentration of the saturated CaCO₃ water solution was 65×10^{-3} kg·m⁻³.

1.3 Experiments on Corrosion Resistance

The corrosion behavior of TiO_2 coatings in corrosive media (strong acid, alkali and salt solutions) with high concentration was investigated qualitatively to test the ability to resist corrosion of heat transfer media. During the corrosion resistance experiments, the test samples were immersed in the corrosive media a certain time at room temperature. The corrosive media included sodium chloride, hydrochloric acid and sodium hydroxide solutions with the concentrations of 25%, 30% and 30%, respectively. After a few hours, the test sample was taken out from the solution to observe its corrosion property.

2 RESULTS AND DISCUSSION

2.1 Characterization of TiO₂-Coated Surfaces

Digital Photos: Fig.1 shows the digital photos of typical test samples for characterization, including untreated and polished surfaces. TiO_2 -coated samples are colorful under natural light, as shown in Fig.1c.



Fig. 1 Digital photos of test samples. (a)Untreated surface;(b) polished surface;(c) coated surface, $\delta=76.8$ nm.

SEM: SEM images of test samples are presented in Fig.2. It can be seen that the surface microstructure of untreated sample is quite rough. While, polished and coated surfaces (Figs.2b~2c) are very smooth. Hence, LPD process does not change the surface morphology of test sample too much.



Fig.2 SEM images of test surfaces. (a) Untreated surface; (b) polished surface; (c) coated surface, δ =76.8nm.

Coating thickness: Figure 3 illustrates typical XRD plots of test samples. In each sub-plot in Fig.3, there are

three obvious spikes showing the existence of substrate material of Cu, and one of them is the highest indicating the largest diffraction intensity of substrate material of Cu. The largest value of diffraction intensity at double diffraction angle for each sample is listed in Table1.

Table1 The largest values of diffraction intensity at double diffraction angle for three test samples.

Polished surface Coated surface Coated surface	
Tonshed surface Coaled surface, Coaled surface,	
δ=18.6nm δ=76.8nm	
2θ , ° I, Counts s ⁻¹ 2θ , ° I, Counts s ⁻¹ 2θ , ° I, Counts s ⁻¹	s ⁻¹
43.28 12357 43.32 12294 43.28 12100	

It is found from Table1 that the largest value of diffraction intensity at double diffraction angle of about 43.28 ° decreases gradually with the increase of the coating thickness. In other words, the highest diffraction peak of untreated substrate is the highest, and that of the coated substrate reduces due to the absorption of part energy of ray. With the increase of film thickness, the amount of absorption of coated film increases, leading to the decrease in height of highest diffraction peak. It is by this difference that the coating thickness of coated samples is measured. The thicknesses of the four TiO₂ films measured were 18.7 nm, 46.7nm, 76.8nm and 108 nm, respectively.

No spike is found on the XRD curve of polished substrate when double diffraction angle is about 25°, as shown in Fig.3a. However, a short spike is observed at about 25° of 2 θ in each XRD plot of coated samples, as shown in Figs.3b and 3c. This short spike represents the diffraction intensity of TiO₂ thin film, and the intensity is different when coating thickness is distinct.

It is noteworthy that the diffraction peak representing TiO_2 coating layer is not obvious. There are two main reasons for this phenomenon. One is that the TiO_2 film is too thin that the spike is also weak, compared to the obvious diffraction peak of substrate material Cu. Another is that the heat treating temperature of test samples is low and crystalline structure of TiO_2 coating is amorphous.





Fig.3 Typical XRD patterns of test samples.
(a)Polished surface; (b) coated surface, δ=18.6nm; (c) coated surface, δ=76.8nm.

Contact angle: Typical digital images of liquid droplets of distilled water and of glycerin on the surfaces of test samples are shown in Fig.4. The contact angle increases sharply when the surfaces are coated with TiO_2 film layers except when the coating thickness is 108nm. No great variations of contact angles can be observed when the coating layer thickness climbing. The contact angle of glycerin is near the same as that of the distilled water.

Table2 shows the measured data of contact angles.

Surface free energy: The physical meaning of surface free energy is necessary work done by overcoming the attractive force between two surfaces, and the values of surface free energy are also shown in Table2. Fig.5 illustrates the relationship between surface free energy and the coating thickness. The values of coating thickness for the untreated and polished samples are both zero. But in order to draw the two bars in the same chart for comparison, we let the thickness value for the untreated sample to be - 10nm in Fig.5.

It can be found that surface free energy of TiO_2 coatings decreases greatly compared to those of untreated and polished surfaces, and it increases suddenly again when the coating thickness exceeds 100nm. This trendy may be related to the effect of nanometer surface.



Fig.4 Liquid droplets of distilled water and glycerin on the surfaces of test samples.
(a)Untreated surface;(b) polished surface;(c) coated surface,δ=18.6nm;(d) coated surface,δ=46.7nm;(e) coated surface,δ=76.8nm;(f) coated surface, δ=108nm.
1-Droplet of distilled water; 2-Droplet of glycerin.

Table2 Measurement results of contact angle and surface free energy of test samples

Test samples of different surfaces	Contact angle of distilled water, $\theta_w/^\circ$	Contact angle of glycerin, $\theta_g/^\circ$	Surface free energy, $\gamma/mJ \cdot m^{-2}$
Untreated	73.13	79.81	37.85
Polished	75.75	82.83	36.39
Coated, 8=18.7nm	93.50	92.67	16.16
Coated, δ=46.7 nm	93.25	93.80	16.74
Coated, δ=76.8 nm	93.25	96.83	18.85
Coated, δ=108 nm	80.75	84.28	27.66



Fig.5 Surface free energy of test samples versus coating thickness.

2.2 The Influence of Surface Modification on Heat Transfer of Pool Boiling of Distilled Water

In order to verify the reproducibility of the experiment data, repeat experiments of pool boiling with distilled water were done on the untreated copper substrate under heat flux of 79.8, 96.6 and 110 kWm⁻². The time interval of the two experiments is two weeks. The results are shown in Fig.6. It can be said that experimental reproducibility is good.

Fig.7 presents the relationship between the pool boiling heat-transfer coefficient on the test surfaces and operation time when heat flux is 96.6 kW·m⁻². Comparing to the data on untreated sample, the heat-transfer coefficients on polished surface are slightly higher. But they are all less than that on TiO₂-coated surfaces, indicating that pool boiling of distilled water is enhanced due to the appearance of TiO₂ coating layer on the copper substrates. However, the relationship between the coating thickness

and the coefficient is not linear. The coefficients on coated surface with thickness of 76.8 nm are the largest, following by those on coated surfaces with thickness of 46.7 nm and 108 nm. The increase of boiling heat transfer coefficient on the surfaces of TiO_2 coating is considered to be due to the growing of the number of active nucleation sites in nucleate boiling heat transfer. But, more visual or direct evidence are needed.



Fig.6 Repeat experiments of distilled water in pool boiling on untreated copper substrate.



Fig.7 Pool boiling heat-transfer coefficient on the test surfaces versus running time.

Meanwhile, the heat transfer coefficients on the coated surfaces with thickness of 46.7 nm and 76.8 nm are quite different even though they are almost equals in the surface free energy (about 20 mJ \cdot m⁻²), which may mean that pool boiling is not only affected by the surface free energy or surface material (since surface free energy depends largely on the inherent property of coating material itself), but also is influenced by the microstructures of coating layers resulted from the difference in coating thickness. And an optimum value of coating thickness or optimum microstructure may exist for the pool boiling enhancement.

2.3 The Influence of Surface Modification on Fouling in Pool Boiling of CaCO₃ Solution

Typical fouling experimental results with heat flux of $96.6 \text{ kW} \cdot \text{m}^{-2}$ are exhibited in Fig.8.

As shown in Fig.8, the heat transfer enhancement is obvious at the beginning of running time when the surface is coated with TiO₂ film layer, and the increase trendy with the coating thickness is the same as that of the distilled water. After a period of time, the coefficient declines sharply due to the deposition of CaCO₃ fouling on the test surfaces and finally reaches a much lower value. The time when the heat transfer coefficient starts to decline (corresponding to end of the fouling induction time in the curve of heat resistance versus time that doesn't show here) is different for distinct test surfaces due to the variation of surface free energy. The turning time for TiO₂ surface coated by LPD is much shorter than that by vacuum evaporation coating even though the enhancement degree of the heat transfer coefficient is relatively higher. Under present experimental conditions, the periods of without fouling deposition for the untreated surface, polished surface and coated surfaces with thickness of 46.7nm, 76.8nm, 108nm are about 400 min, 700min, 4000min, 3500min and 1600min, respectively. However, for vacuum evaporation coating surface, it exceeds at least 4000min, and the durability experiment of coated surface with thickness of 80nm shows that it can reach a value of 13000min (Wang, et al., 2007). This indicates that the coating method may affect heat transfer and fouling behavior greatly.

It can also be expected from Fig.8 that the fouling heat resistance rises near linearly with the prolonging of operating time, which agrees with the published work in open literature.



Fig. 8 Heat transfer coefficients versus operation time on different test surfaces in pool boiling of CaCO₃ solution.

A surface with high free energy always tends to absorb certain dirt to reduce its surface free energy. With time running, the thickness of fouling layer climbs, and heat resistance also increases, leading to a reduction of heat transfer coefficient and ultimately reaching to a stable low value. On the surface with lower surface free energy, fouling is more difficult to deposit, and fouling induction period is enlarged.

The fouling induction period refers to the time length starting from the contact between the clean surface in heat exchanger and the solution to the time when the deposit was able to be detected (Yang, et al.,2004). This period may last anytime from few seconds to several days. Before the induction time, the initially high heat transfer coefficients remain unchanged. During this time, a few nuclei for crystallization are formed and scattered on the heat transfer surface. Generally, no induction period occurs for particulate fouling. If the measuring method is enough sensitive, fouling of surfaces under pool boiling should not show induction period. However, the induction time is influenced by many factors such as concentrations of solutions, fouling types, states of heat transfer surfaces, surface temperature, measuring accuracy of sensor, etc. For super-saturation solution of $CaCO_3$ in pool boiling, the rates of nucleation and growth of crystallization are not infinite. Hence, a fouling induction period can occur on the untreated surfaces for the pool boiling system (Ren, et al., 2001), as shown in Fig.8.

For pool boiling of water, the values of heat transfer coefficients in this work are lower than those reported in literature. There are maybe several reasons for this. One relates to the system error of experimental apparatus. There so many factors affect the final results of coefficients, such as the geometry shape of boiling surface or sample (such as tube and plate), water pool size and shape, operation and environment conditions, measurement methods of parameters of temperature and heat flux. For different authors, the difference in magnitude of heat transfer coefficient of pool boiling can reach 20 times. Another one may relate to the neglect of heat conductivity of coating material on the heat transfer surface. The third one may be the error of heat flux calculation.

Fortunately, the relative values of boiling coefficients and the comparison results between different surfaces are more important. Keeping this in mind, the results of heat transfer coefficients are still meaningful. A measure that uses another type of pool boiling apparatus will be taken to test the issue of datum difference from most reported literature.

2.4 Anticorrosion Property of Coated Surfaces

Experimental results of corrosion resistance are shown in Table 3. Digital images of surface topography of samples before and after corrosion experiment are shown in Fig.9.



.9 Digital images of test samples before and after experiments of corrosion resistance.

(a) Before corrosion experiment; (b) After 600 hours in 25% NaCl solution; (c) After 100 hours in 30% HCl solution; (d)After 200 hours in 30% NaOH solution.
 1-Coated; 2-Untreated.

Table? Degults of corregion registence experime	
TADIES RESIDE OF COTOSION RESISTANCE EXPERIME	ents

Corrosive	Immersion	mersion Description of experimental results	
incuta	una unic, nours	Untreated surface	Coated surface
25% NaCl solution	600	Slight corrosion (Fig.9b2).	No corrosion after 200 hours and coated film was eroded and original surface of substrate was observed until after 600 hours (Fig.9b1).
30% HCl	100	Serious	Serious corrosion with dark

solution		corrosion with dark surface (Fig.9c2).	surface (Fig.9c1).
30% NaOH solution	200	Serious pit corrosion (Fig.9d2).	No coating breakage was found for coated surface, and serious pit corrosion was seen on uncoated surface (Fig.9d1).

The experimental results indicate that both coated and untreated test samples are easy to be corroded in acidic solution environment, and the coating layer does not improve the character of corrosion resistance. In alkali solution environment, the behavior of corrosion resistance of coated sample is better than that of untreated sample in the experimental period. In the salt solution, coated film can resist corrosion until after 600 hours.

Much work is needed to examine the accurate value of pool boiling coefficient and to verify the existence of the induction period in pool boiling.

3 CONCLUDING REMARKS

Liquid phase deposition was successfully used to coat TiO_2 film layer in nanometer order on red copper substrate. Pool boiling heat transfer and fouling experiments were carried out with distilled water and $CaCO_3$ solution as work fluids. In addition, the qualitative experiments of corrosion resistance on these coated surfaces in acid, alkali and salt solutions with high concentrations were also performed.

- Pool boiling is enhanced and fouling induction period is enlarged on the coated surfaces. The key factors that influence pool boiling heat transfer and fouling are the surface free energy, microstructure and coating method. An optimum value of coating thickness or optimum microstructure may exist for pool boiling enhancement and antifouling.
- 2. Under present conditions, coated surface can resist corrosion in certain degree in alkali and salt solution environments. This promising work may help us to find a new multi-function heat-transfer surface, which is crucial for energy saving in process industries.
- 3. One further topic should focus on detailed investigations on antifouling and heat transfer enhancement mechanism. Another is to find new coating materials that can also stand against acidic environment. Of course, new surface modification method is also needed to improve the durability of the coatings.

NOMENCLATURE

- *h* heat-transfer coefficient in pool boiling, $W \cdot m^{-2} \cdot K^{-1}$
- I XRD integrated intensity, counts s^{-1}
- q heat flux, $W \cdot m^{-2}$
- t time, min
- γ surface free energy, J·m⁻²
- δ thickness of coating layer, nm
- θ contact angle, °
- diffraction angle, °

Subscript

- g glycerin as test liquid
- *w* distilled water as test liquid

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