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Heat Transfer Enhancement in Condensers in Steam Turbine Based Combined Heat and Power Plants

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Today one major challenge is the enhancement of heat transfer in condensers of modern steam-turbine plants. If one shifts from traditional film condensation to dropwise condensation, the heat transfer coefficient on the steam side of the condenser's tubes significantly increases thanks to the hydrophobization of the external surfaces of the condenser's tubes. The results of laboratory tests and tests in situ, which have been conducted earlier, provide evidence that hydrophobization of those brass tubes that have been supplied with rather smooth surfaces, with the use of a surface-active film-forming agent belonging to the aliphatic amines class allows to increase the condenser's heat transfer coefficient by half or even more. This work is devoted to enhancement of heat transfer in condensers of steam-turbine plants through the use of a superhydrophobic effect with preparation at the first stage of a hierarchical double rough structure on brass surfaces with the use of the method of alternating current electrochemical etching in the phosphoric acid. It has been shown for the first time that modern technologies for achieving superhydrophobicity based on treatment of brass surfaces with octadecylamine, a surface-active film-forming agent belonging to the aliphatic amines class acting as a hydrophobizer, allows to achieve contact angles at the level of 150°.

Key words: Condensers of steam-turbine plants, Heat transfer, Corrosion, Cycle efficiency, Heat transfer coefficient, Hydrophobization, Superhydrophobic effect and Surface-active agent.

Today one major challenge is the enhancement of heat transfer in condensers of modern steam-turbine plants because even in case of off-design behavior of a such a system high values of heat transfer coefficient allow, first of all, to ensure high performance, i.e. maintain the necessary vacuum level in the condenser' steam space (it is noteworthy to mention that in general impairment of vacuum by 1 kPa leads to a decrease of performance of the steam turbine system by 1%), and, secondly, to create conditions for a greater degree of deaeration thus minimizing the corrosion in the condensate-feed tract.

Today there is a huge database in the technical literature for the heat exchange intensification. It contains more than 10,000 technical articles, papers and reports that have been published in numerous periodicals and bibliographical records AE Bergles *et al*[1,2] MK Jensen and B. Shome[3] RL Webb reviews[4, 5], DP Shatto and JP Peterson[6] and others.

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transfer coefficient on the steam side of the condenser's tubes significantly increases thanks to the hydrophobization of the external surfaces of the condenser's tubes. This effect is due, first of all, to the decrease in the thermal resistance of the liquid film (the width of the film on the surface of a tube might reach a hundred microns or even several millimeters; instead of the film individual droplets are being formed and they intensively slide down the cylindrical surface of the tube into the intertubular space so that the metal surface is being uncovered). Besides it, due to additional *dispergation of the liquid phase in the quasi-dropwise flow in the intertubular space the interphase heat transfer is being enhanced thanks to the increase in the area of the surface of contact between the two phases and as a result the condensate depression (overcooling) is reduced and the cycle efficiency is increased.*

According to the modern classification, hydrophilic materials are defined as materials, whose contact angle (the angle between a droplet's edge and the surface underneath it), is either equal to zero or less than 90°. Contact angles of hydrophobic materials lie in the range from 90° to 180°. If the contact angle is equal to 180° (absolutely nonwettable material), the droplet must contact the surface only in one point; however, this is only a theoretical assumption that never occurs in practice.

Over two hundred years ago Thomas Young has shown in his classical paper titled «An Essay on the Cohesion of Fluids» that in equilibrium the macroscopic contact angle for a fluid droplet on a solid surface *[phi]*$_0$ is a thermodynamic characteristic that can be expressed in terms of other thermodynamic parameters of the system: solid-vapor interfacial energy *[sigma]*$_{sv}$, solid-liquid interfacial energy *[sigma]*$_{sl}$ and vapor-liquid interfacial energy *[sigma]*$_{lv}$.

$$\cos \theta_0 = (\sigma_{sv} - \sigma_{sl}) / \sigma_{lv} \qquad ...(1)$$

This equation that is called the Young's equation shows that in order to change the contact angle of wetting it is sufficient to change the properties of subsurface layers that are only several nanometers thick as they determine proper surface energy. In fact contact angles can be greater than 90° (i.e. the cosine of such a contact angle can be negative) only in case of solid surfaces with low *[sigma]*$_{sv}$. However, in case of most structural materials, for example, metals and their oxides, the surface energy is rather high. In order to reduce it one can coat the surface of such materials with a few nanometers-thick layer of a hydrophobic agent, i.e. a substance characterized by low surface energy.

For example, the results of laboratory tests and tests in situ, which have been conducted earlier[7-9], provide evidence that hydrophobization of those brass tubes that have been supplied with rather smooth surfaces, with the use of a surface-active film-forming agent belonging to the aliphatic amines class, i.e. octadecylamine (ODA), allows to increase the condenser's heat transfer coefficient by half or even more.

In this case the contact angle of wetting increased from 79° to only 109-111°. However, it is still unclear, if it is possible (and if yes, to what extent) to enhance the heat exchange through further increase of the contact angle of wetting.

One particular kind of hydrophobic materials is the superhydrophobic materials for whom the effective contact angle is not less than 150°. Superhydrophobicity attracts considerable attention due to important practical applications. The so-called "lotus effect" is a classical model of self-cleaning. The lotus leaves are covered with micro/nano-structures inspiring researchers to create artificial superhydrophobic surfaces imitating the lotus leaves.

In general the preparation of superhydrophobic surfaces comprises two stages: at the first stage one has to rough-texture the surface, at the second stage the surface must be modified in order to ensure low surface energy[10-13].

The roughness of the wetted surface influences the measured contact angle so that the contact angle for a rough surface differs from that for a smooth surface. In general, there exist two main wetting regimes: homogeneous wetting regime (Wenzel model)[14], when the liquid fills in the roughness grooves of a surface, i.e. contacts with the entire surface (Fig 1,a), and heterogeneous wetting regime (Cassie–Baxter model [15]), when surface is a composite of two types of patches, in most cases such patches being air and solid (Fig. 1,b).

Both wetting regimes can be characterized by such parameters as effective contact angle and Young contact angle. The effective contact angle *[phi]* is the angle between the droplet meniscus and the surface associated with the surface of a solid body as a whole. The Young (contact) angle *[phi]*$_0$ is the local angle between the droplet meniscus and the solid surface in the zone where three phases meet. According to equation (1), the Young angle is determined, first of all, by the chemical composition of the contacting surfaces. In case of a homogeneous wetting regime the effective contact angle with a rough surface can be calculated based on the Derjaguin-Wenzel equation:

$$\cos\theta = (S/S_0)\cdot\cos\theta_0 = r\cdot\cos\theta_0 \qquad ...(2)$$

where $r = S/S_0$ is the roughness ratio, which is equal to the *ratio* of true area of the solid *surface* S to the *apparent* area S_0. Based on equation (2) one can conclude that in case of a homogeneous wetting regime the roughness of the surface results in increasing the contact angle of hydrophobic surfaces with *[phi]*$_0$>90° and reducing the contact angles of hydrophilic surfaces with *[phi]*$_0$<90°.

In case of heterogeneous wetting regimes when the liquid-solid interface is heterogeneous being comprised of patches of solid with contact angle equal to 90° and cavities fully or partially filled with air (see figure 1,b), the effective contact angle is calculated based on the Cassie-Baxter equation:

$$\cos\theta = f\cdot r_f\cdot\cos\theta_0 + f - 1 \qquad ...(3)$$

Where f is the fraction of solid surface area wet by the liquid, r_f is the roughness ratio of the wetted surface. If $f \to 1$ the wetting mode shifts from the heterogeneous regime to the homogeneous regime, and equation (3) becomes equation (2), and $f \to 0$ corresponds to the absolutely nonwettable material surface. The analysis of equation (3) provides evidence that in case of a heterogeneous wetting regime the smallness of the fraction of the solid surface area that really contacts the liquid is one of the key factors determining the properties of superhydrophobic materials and coatings.

A homogeneous wetting regime can shift to a heterogeneous wetting regime if primary droplets are formed via condensation of a

Table 1. Shape of samples and methods of preparation of the surface

S No.	Shape of sample	Material	Method of preparation of the surface	Type of sandpaper used in compliance with ISO-6344
1	Plate (size 30×40 mm)	Brass L63	Cleaning and roughening both in longitudinal and transverse direction	P-180
2	Plate (size 30×40 mm)	Brass L63	Cleaning and roughening both in longitudinal and transverse direction	P-180

Table 2. Results of measurement of the roughness of surfaces after roughening with sandpaper P-180

S No.	Sample's side No.		Profile No.	Ra, µm	Rz, µm	Rt, µm	Area assessed
1	1	longitudinal_center	p1	0,3	3,5	10,2	length 11000 -21000 µm
		transverse_center	p2	0,3	2,7	3,0	length 8500 – 18500 µm
	2	longitudinal_center	p1	0,3	3,1	4,3	length 11000 – 21000 µm
		transverse_center	p2	0,3	3,4	4,9	length 8500 – 18500 µm
			average	0,3	3,2	5,6	
2	1	longitudinal_center	p1	0,5	4,6	6,3	length 11000 – 21000 µm
		transverse_center	p2	0,5	5,8	8,3	length 8500 – 18500 µm
	2	longitudinal_center	p1	0,3	2,9	4,9	length 8500 – 18500 µm
		transverse_center	p2	0,5	5,6	8,7	length 8500 - 18500 µm
			Average	0,5	4,7	7,1	

supersaturated vapor on a cooled hydrophobic surface. This case is of great significance for evacuation of droplets from cylindrical surfaces of the condensers of steam-turbine plants, if such surfaces are preliminarily hydrophobized.

When considering the process of condensation of vapor in condensers of steam-turbine plants, it is noteworthy to mention that in practice even in case of a rather high degree of deaeration of the vapor (in case of combined heat and power plants the maximum allowable concentration of oxygen is equal to C_{02}=20 µg /kg) the concentration of non-condensed gases near the wall of the tubes is markedly greater. This is because only vapor is being condensed on the cold wall, and the air remains. According to the Dalton's law, in a mixture of non-reacting gases the total pressure p_0 is equal to the sum of the partial pressure of vapor p_v and the partial pressure of the air p_a, i.e. $p_0 = p_v + p_a$. As a result of the condensation, near the wall the pressure of vapor p_v is lower than in the other parts of the volume. Therefore p_v continuously decreases in the direction of the wall and the nearer the wall the more rapid is the decrease; in contrast near the wall p_a increases.

Consequently, near the wall the concentration of the air is large, so in this region the air can be regarded as a layer through which the molecules of vapor are being diffused. Such phenomena lead to the decrease of the temperature drop $\Delta t = t_s - t_l$, because the temperature of the mixture is always equal to the vapor saturation temperature at partial pressure p_v. As p_v is always lower than p_0, the temperature t_s will be always lower than the temperature of saturation of the vapor, whose pressure is equal to the total pressure in the mixture p_0.

At the same time, in case of a hydrophobic surface with necessary roughness level the presence of non-condensed gases near the wall increases the probability of formation of a heterogeneous wetting regime, namely in case of a shift from film condensation to dropwise condensation the contact of droplets with a rough surface leads to creation of favorable conditions,

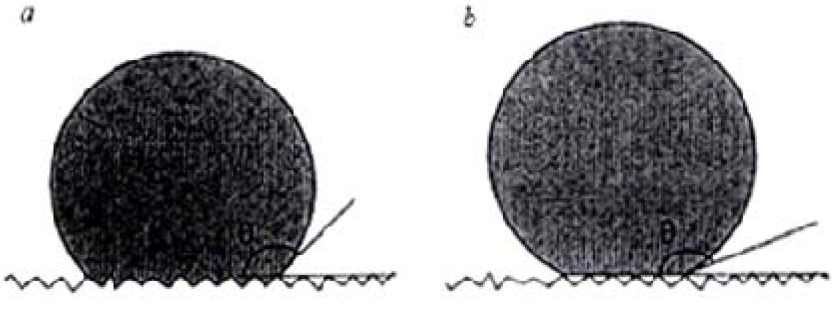

Fig. 1. Homogeneous (a) and heterogeneous (b) wetting regimes

Table 3. Results of measurement of contact angles using brass samples treated with ODA

S No.	Sequential number of measurement	Contact angle *[phi]*, degree from the left side of the drop *[phi]*$_l$	from the right side of the drop *[phi]*$_v$	average value (*[phi]*$_l$+ *[phi]*$_v$)/2	final average value *[phi]*
1	1	151,37	151,17	151,27	149,13
	2	149,65	149,56	149,61	
	3	147,21	145,80	146,51	
2	1	147,76	147,65	147,71	145,08
	2	140,81	139,91	140,36	
	3	147,54	146,80	147,17	

when in the contact area the surface is wetted only partly, i.e. the contact angle is increased to the maximum extent possible.

At present in the literature authors describe a great number of methods used in laboratories for producing surfaces with necessary multimodal roughness[10].

The two main approaches to production of hydrophobic surfaces are the roughening of surfaces using various procedures and the formation of nanoscopic layers of hydrophobic substances on the surfaces to be modified.

One method of producing brass surfaces with necessary roughness is chemical etching[16], using as etchant a mixture of iron chloride **and** hydrochloric acid. In order to prepare the necessary double structure of the metal with nanoscopic asperities, first of all, a sequence of lines is drawn on the surface, said image being incised through etching. Then the surface is fluoridated with the use of *ethoxysilanes and air dried*.

A mixture of acids such as hydrochloric, nitric and hydrofluoric acids in certain proportions can be also used as an etchant[17]. At the first stage of the formation of a certain structure on the surface the brass samples are cleaned and polished. At the second stage the double structure is being formed through etching in a mixture of acids. The final stage is the formation of a film of a material with low surface energy on the surface with the use of *stearic acid ethanol solution* at room temperature.

Another method of preparation of a hierarchic double structure on a brass surface is the use of alternating current electrochemical etching in a phosphoric acid solution[18]. Before being etched brass sheets/ plates are immersed into acetone and cleaned with the use of ultrasound and then mechanically polished with sandpaper 180# and rinsed with deionized water. The hierarchic structure is formed on the surface in the process of alternating current electrochemical etching in the phosphoric acid. Then the surface of the samples is modified with the use of stearic acid and air dried.

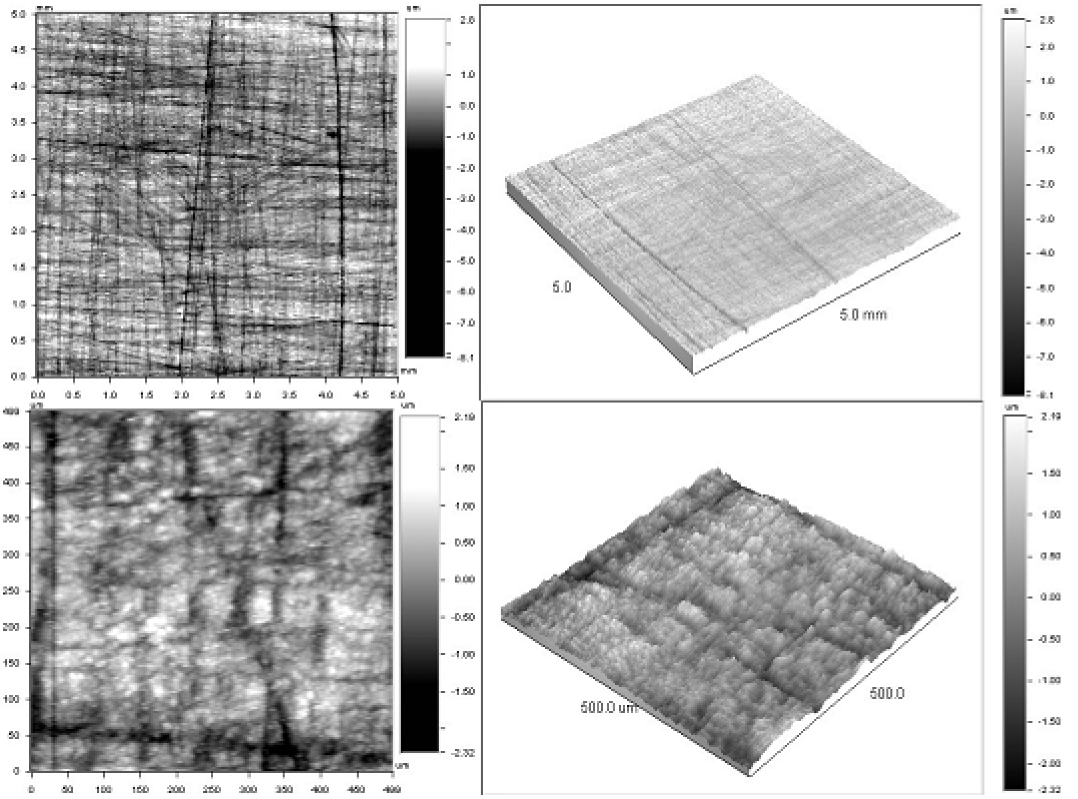

Fig. 2. 3D map of the surface of sample No. 1 after treatment of the surface with ODA

Purpose of the experiment

This work is devoted to enhancement of heat transfer in condensers of steam-turbine plants through the use of a superhydrophobic effect with preparation at the first stage of a hierarchical double rough structure on brass surfaces with the use of the method of alternating current electrochemical etching in the phosphoric acid described in[18], and achievement at the second stage of the necessary low surface energy with the use of octadecylamine (ODA), a surface-active substance, instead of stearic acid. This surface-active substance has been selected, first of all, because its thermophysical properties, as well as *concomitant effects influencing the operation of heat-power equipment* have been studied in detail in a number of fundamental and applied researches[19,20]. In particular, it has been shown that in case of oriented adsorption of ODA molecules on the surface of metals (including brass when the polar group is oriented toward the most polarized solid phase and the hydrocarbon radical is oriented toward the water (or vapor) phase) a one-molecule thick film is being formed as a Langmuir film (sometimes called *Langmuir's fence*). As a result the surface energy at the interface of phases $ó_{sv}$ decreases by several times and, consequently the surface becomes more hydrophobic. Octadecylamine is widely used in heat-power equipment of combined heat and power plants; in particular, it is used for protection against corrosion of internal surfaces of water-vapor ducts and conduits including tubes and pipes of steam generators, turbines, condensers, condensate feed systems, regeneration systems, pumps, tubings, fittings and fixtures in compliance with the applicable guidelines of the Russian Federation titled «Guidelines for conservation of heat-power equipment with the use of film-forming amines», Russian Federation 34.20.591-97.

Preparing and conducting experiments

Two brass samples were cleaned and roughened with sandpaper. Table 1 below presents data on the preparation of these brass samples.

Table 2 shows the results of measurement of surface roughness.

The prepared samples were immersed into acetone and cleaned with the use of an ultrasonic bath at the temperature of 25-30 °C during 10 minutes.

Then the samples were rinsed with deionized water.

Both samples were attached to wires and placed into a bowl with 0,5M solution of orthophosphoric acid and the wires were connected to an ac power source 20V 50 Hz. The samples were parallel to each other. They were etched during 5 minutes. Then the samples were taken away and rinsed with deionized water.

After being etched the samples were immersed into ODA emulsion $C_{ODA} = 30$ mg/kg) placed over a boiling water bath and there they remained at a temperature of 90°C during 8 hours. Then the samples were taken away and dried at room temperature. Then contact angles were measured.

RESULTS

Fig. 2 shows a 3D-map of the surface of a sample after treatment with ODA. Table 3 presents the results of measurement of contact angles after treatment of a brass surface.

The contact angles were measured on one sides of the treated samples because when this method is used, it is the surfaces facing each other that become superhydrophobic. The contact angles were measured with optical tensiometer OCA 20 (Germany). The measurements of contact angles were made on the droplets of volume of 20 µl, as smaller droplets could not be placed on the sample because they could not "catch hold" of the surface and hung on the syringe.

DISCUSSION

Finally we can make the following conclusions based on the results of work:

1. In case of condensers of steam-turbine plants superhydrophobicity of external surfaces of brass tubes facilitates the shift from a homogeneous wetting regime to a heterogeneous wetting regime, when the surface in the contact area is wetted only partly and, to all appearances, this might additionally enhance the heat transfer. However, the last assumption must be experimentally proved.
2. It has been shown for the first time that modern technologies for achieving superhydrophobicity based on treatment of brass surfaces with octadecylamine, a surface-active film-forming

agent belonging to the aliphatic amines class acting as a hydrophobizer, allows to achieve contact angles at the level of 150°.

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