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LARGE-SCALE PLASMA POLYMER COATING ON HEAT EXCHANGER FINS FOR IMPROVING THE WETTABILITY

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ABSTRACT

This research presents the results of the recently developed large-scale hydrophilic polymer coating by plasma polymerization, optimum plasma zone (OPZ) process. The excellent hydrophilicity of heat exchanger fin surface could give good effects to efficient drainage of condensate water as well as heat transfer performance. The hydrophilicity of layer treated by large-scale OPZ system is excellent irrespective of line speed from 0.6 m/min to 2.4 m/min. The good lateral uniformity of the hydrophilicity could be acquired in large scale OPZ treatment. The application of OPZ technique to the heat exchanger could enhance the efficiency of heat transfer, resulting from decrease of pressure drop. Due to long-term durability of hydrophilicity, the heat transfer performance improved by OPZ process cannot be deteriorated with operation cycle.

INTRODUCTION

Need for hydrophilic surface modification of metal is increasing in applications such as heat exchanger, printing, and adhesion of metal to other material, etc. In the application fields of heat exchanger, the water is condensed in the form of droplet on the hydrophobic metal surface with native oxide. The condensate of droplet may cause bridging between fins in heat exchanger of air-conditioner, leading to increase in the air-side pressure drop (Hong et al., 1999, and Min et al., 2000). Also, the problem of the condensate carryover can occur in the droplet formation on the hydrophobic surface (Min et al., 2001). Consequently, the use of hydrophilic surface can reduce the air-side pressure drop, and diminish the condensate carryover, resulting in increase the heat transfer performance (Kim et al., 2002).

Up to date, the surfactant coating is widely used to make metal surface with native oxide hydrophilic. However, there is a big problem of the loss in hydrophilic property with operation, due to the solution of surfactant in water. That is, the improvement of heat transfer performance could be expected at initial stage by use of surfactant coating, but the heat transfer performance would be deteriorated with operation cycle (Ha, et al, 1998). In order to solve the problem in surfactant coating, the development of new surface modification technique have been required to have the characteristics of the good hydrophilicity and non-aging property in water. Optimum plasma zone (OPZ) process recently developed by Koh and his co-workers can satisfy these requirements (Choi et al, 2000). OPZ process utilizes the plasma state to successfully make the hydrophilic polymer films on the metal surface. The advantages of OPZ process are following as; (a) excellent hydrophilicity, (b) good adhesion, (c) high chemical resistance, (d) simple process, and (e) environmental-friendly process (Yasuda et al., 1985).

In order to apply OPZ technique to the industry, the system to realize OPZ technique uniformly in large-scale area is inevitably necessary. For large area coating of hydrophilic polymer, the treatment must be homogeneously over, laterally, considerable distances. In this study, the hydrophilic property of OPZ-treated Al surface and its adhesion to metal would be introduced. The hydrophilicity of Al treated by large scale OPZ system would be discussed in terms of line speed, uniformity, and long-term durability. Effects of the OPZ hydrophilic layer on the heat transfer performance and aging property would be investigated with the heat exchanger of Al fin treated by large scale OPZ system.

EXPERIMENTAL

Optimum Plasma Zone Process

Optimum plasma zone (OPZ) is the process that could deposit hydrophilic polymeric thin films on the metal using plasma of specific mixture gases. OPZ system consists of three parts; vacuum formation components, gas delivering system, and DC power supplying units. OPZ process for hydrophilic layer coating on metal includes : (1) positioning anode and cathode electrodes in a vacuum chamber, (2) maintaining the pressure in the chamber at 10^{-3} Torr, (3) supplying a reaction gases of C_2H_2 and N_2 to specific pressure, (4) applying a voltage to the electrodes to form plasma, and (5) sustaining plasma state to deposit hydrophilic polymeric films on metal.

The schematic diagram of the batch-type OPZ system is shown in the Fig. 2. The OPZ system mainly consists of three parts; (a) DC power applying part, (b) gas feeding part, and (c) pumping unit. Samples were positioned at anode electrode place. The vacuum chamber was evacuated by a rotary pump, a molecular booster pump, and a diffusion pump. The mixture gases for polymerization were introduced up to the pressure of a predetermined value. Plasma was generated under appropriate vacuum condition by applying DC power. Applied bias was changed from 0.6 to 1 kV.

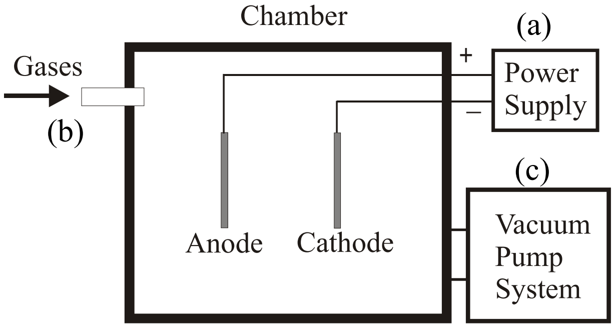

Fig. 1 Schematic diagram of batch type optimum plasma zone system.

Large Scale OPZ Equipment

Fig. 2 shows the photographs of large scale OPZ system. This system mainly includes the winding chamber, process chamber, and unwinding chamber. Al roll sheet with width of 600 mm is installed in unwinding chamber, and Al sheet can be moving at the line speed of 0 to 12 m/min. The process chamber has the gas distribution component, and four cathode electrode sets. The number of gas supplying outlet in distribution component is 16, and each outlet is positioned by the design for the uniform supply of gas. Cathode electrode is specially designed for continuous use in DC plasma polymerization system, and has the area of 200 mm × 700 mm. The system is evacuated to below 10^{-3} Torr by rotary pump and molecular booster pump. Working pressure is changed from 100 mTorr to 500 mTorr. The pressure is automatically controlled to set value by the throttle valve transmitted signally with the pressure gauge. DC power supply of 3 kW is connected to each cathode electrode, and Al sheet operates as anode electrode.

(a) **(b)**

Fig. 2 Photographs of large scale OPZ system; (a) side view, and (b) front view of opened system.

Process data of large scale OPZ system are summarized in Table 1.

Table 1 Process data of large scale OPZ system.

Vacuum degree	> 10^{-3} Torr
Line speed	0 ~ 12 m/min
Cathode electrode	200 mm × 700 mm, 4 ea
Active plasma area	700 mm × 800 mm
DC power supply	12 kW
Substrate	600 mm wide Al roll sheet

Characterization of Hydrophilic Layer

The hydrophilicity of polymer surface was investigated with the water contact angle. The static contact angle measurement was conducted using contact angle meter (Tantec Co.; CAM-micro) to investigate the hydrophilicity of metal surface treated by OPZ process. Contact angles of twenty points per each specimen were acquired and the average contact angle was calculated. The deviation of contact angles was about 2~3°. In order to analyze the chemical state of polymeric surface on metal deposited by OPZ, X-ray photoelectron spectroscopy (XPS) was performed using a Surface Science Instrument 2803-S spectrometer which had a base pressure of 2×10^{-10} Torr. Scanning electron microscope (SEM) was used to examine the surface morphology of hydrophilic layer by OPZ. The adhesion of plasma polymer to metal was checked by using boiling test in which each sample was dipped into boiling water for specific time. Adhesion performance of paint to metal was evaluated by the tape peel test according to the American Society for Testing and Materials (ASTM 3359 B). This test method gives semi-quantitative results classified in grades 0 to 5, in which 5 means that the tape cannot peel off the film.

Plate Fin-Tube Heat Exchanger using Al Fin by OPZ

Schematic diagram of experimental apparatus is shown in Fig. 3. The system of experimental apparatus consists of three independent parts; a water supply loop, a psychrometric chamber, a wind tunnel. Water supply loop has constant water bath, heater, 2HP stainless steel pump, and two mass flow metes. The psychrometric chamber includes an air handling unit and an air sampling unit. Wind tunnel based on ASHRAE standard includes nozzles from which air flow rate is measured (ASHRAE 1987 and 1992). Entrance and exit dry/wet bulb temperature are measured by RTD (Pt 100 Ω) sensor with accuracy of 0.05 °C. The data are collected and sent to data acquisition system.

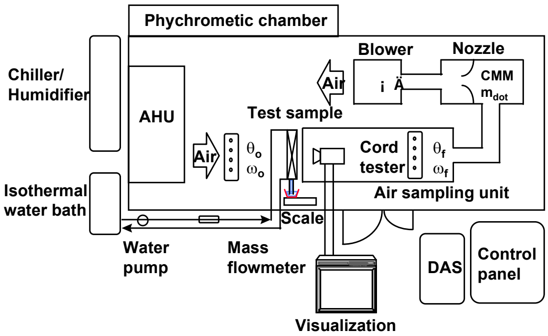

Fig. 3 Schematic diagram of experimental apparatus

Test samples for plate fin-tube heat exchanger for air conditioning system has typical structure and consist of aluminum fin and ϕ 7 mm grooved copper tube with staggered arrangement. In order to compare the performance of heat exchanger with different fin surfaces, the heat exchanger of three types were prepared: the fin-tube heat exchangers using (1) bare Al fin without any treatment, (2) surfactant-coated Al fin, and (3) OPZ-treated Al fin. The test conditions are listed in Table 2.

Table 2. Test conditions for fin-tube heat exchanger performance.

Air	Inlet dry bulb temp., °C	27
	Inlet wet bulb temp., °C	19.5
	Frontal air velocity, m/s	1.5
Water	Inlet temperature, °C	5.0
	Flow rate, kg/h	200 ~ 550
	Reynolds number	> 10,000

RESULTS AND DISCUSSION

Hydrophilic Layer by OPZ

Contact angle. In order to examine the hydrophilicity of layer by OPZ, the contact angle of plasma polymer was measured. The effect of nitrogen ratio in mixture gas on the wettability of plasma polymer was investigated, and its results are shown in Fig. 4. The contact angle of bare Al surface without any treatment is 90°, the contact angles of plasma polymerized Al surface ranges from 42° to 23° with the change in the ratio of nitrogen gas to mixture gas, R_N. As the R_N increases, the contact angle of OPZ layer decreases. Nitrogen gas cannot be polymerized by itself in plasma state. However, the nitrogen can participate in polymerization when mixed with polymerizable gases such as hydrocarbon, fluorocarbon.

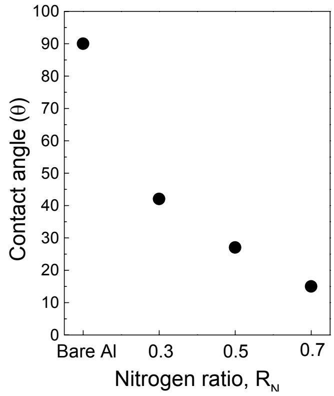

Fig. 4 Contact angles of Al surfaces polymerized by OPZ with nitrogen ratio in gas mixture, R_N.

At this time, the nitrogen is incorporated in plasma polymer to form carbon-nitrogen bonds that reveals the hydrophilicity. According to compositional analysis of plasma polymer with R_N, the higher R_N is, the more nitrogen is incorporated in polymer layer, leading to more wettable characteristics.

XPS result. The chemical state of OPZ-layer surface was investigated by XPS analysis. Fig. 5 shows the XPS spectra obtained from the plasma polymer at R_N of 0.7. As shown in Fig. 5, the Cls peak has asymmetric shape, indicating that there are other peaks in C1s peaks, except bonds of –C-C-/-C-H- located at 284.6 eV. Asymmetric shape of C1s would be attributed to the existence of bonds with binding energy higher than 284.6 eV. When considering the C1s peak with N1s and O1s peaks, possible bonds of binding energy above 284.6 eV in Cls of plasma polymer could be assigned to –C-O-, -(C=O)-, -C=N-, and C-N, which act as the hydrophilic groups. Consequently, it is known that the C1s core level spectra consists of the main peak of –C-C-/-C-H-, and peaks of hydrophilic groups such as –C-O-, -(C=O)-, -C=N-, and C-N. Even though oxygen gas is not included at plasma polymerization process, oxygen is detected on the polymer surface by XPS. The formation of bonds containing oxygen could be explained by following as. There are quite amounts of free radicals in plasma polymer even after the end of plasma polymerization process. When plasma polymer is exposed to an air, the free radicals on plasma polymer can react with oxygen in air. Therefore, the inclusion of oxygen is generally considered to be a result of the post reaction of trapped free radicals with ambient O_2. Since carbon-oxygen bonds created by post reaction are hydrophilic groups, the post reaction of plasma polymer in air could be advantageous to the application requiring the wettability.

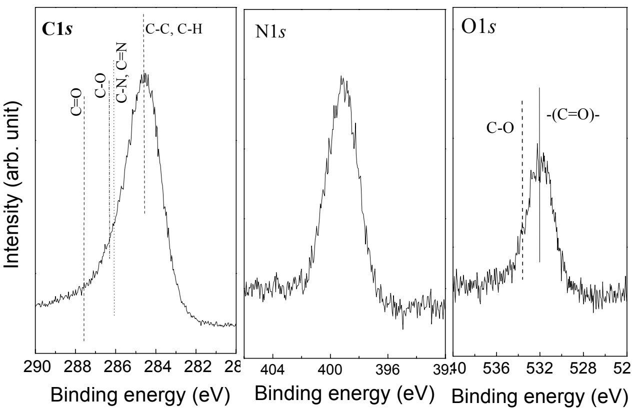

Fig. 5 XPS core level spectra of hydrophilic plasma polymer obtained at R_N of 0.7.

Adhesion of OPZ Layer. The adhesion of hydrophilic layer by OPZ to metal is very important to adopt this technique to industrial applications. If the adhesion of layer to substrate were poor, it would be difficult for layer to be used in the real products due to its short lifetime. Both plasma polymers obtained at anode and cathode electrode all passed dry tape peel test. So, the adhesion of plasma polymers at anode and cathode was evaluated by boiling test. Fig. 6 shows the adhesion results of plasma polymer identified by the boiling test that is one of the most severe adhesion tests.

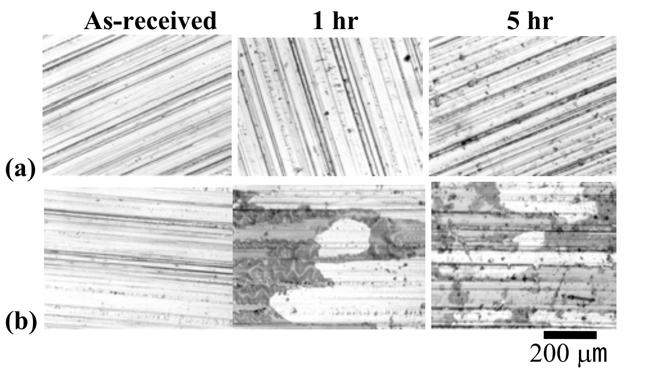

Fig. 6 Optical microscope photographs of plasma polymers at (a) anode and (b) cathode electrode with boiling time.

As shown in Fig. 6(b), plasma polymer obtained at cathode electrode was buckled in some parts after boiling of 1 hour, and was partially removed in boiling of 5 hours. In the contrary to the results of cathode plasma polymer, no peeled or buckled parts on plasma polymer at anode were found even after boiling of 5 hours. This indicates that the adhesion of anode-plasma polymer to Al surface is so strong that there is no problem in the application of anode plasma polymer to various real products.

Large Scale Continuous OPZ System

The important things in large-scale system are the properties with production speed, the uniformity, and the durability in order to make a mass production successful. In this section, the properties of layer obtained by large-scale continuous OPZ system would be discussed from the point of views of the line speed, the uniformity and the durability.

Contact angle and surface morphology. Fig. 7 shows the contact angle of Al treated by OPZ with line speed. Contact angles of OPZ treated Al ranged from 15° to 22° with the change of line speed. Although there is a slight increase of contact angle with line speed, all surfaces obtained large scale OPZ reveals very good hydrophilicity, irrespective of line speed.

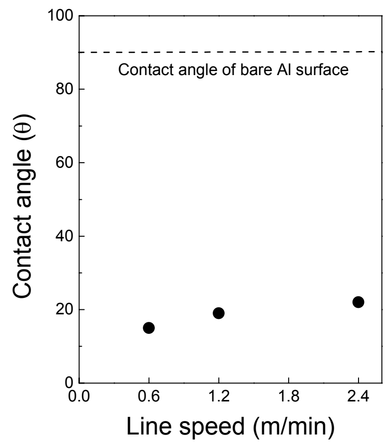

Fig. 7 Contact angle of Al treated by OPZ with line speed.

The surface morphology of OPZ treated Al as a function of line speed was investigated by SEM, and is shown in Fig. 8. The particle size of polymer surface decreased with increase of line speed. As the line speed increases, the residence time of Al sheet in active plasma zone decreases, leading to the reduction of deposition time. In batch type OPZ system, the particle is observed to grow with increase of deposition time. Therefore, it is considered that the change of particle size with line speed would be attributed to the resident time of Al surface in active plasma zone.

Since the system used in this study is pilot plant scale, the productivity is relatively low. However, if the scale of system were increased with the enlargement of active plasma zone, the treatment speed, productivity, could be increased as much as the industry needs. For example, LG electronics adopted this technology for producing the residential air-conditioner, established the mass production system of OPZ treatment, and have produced the air-conditioner installing the heat exchanger treated by OPZ.

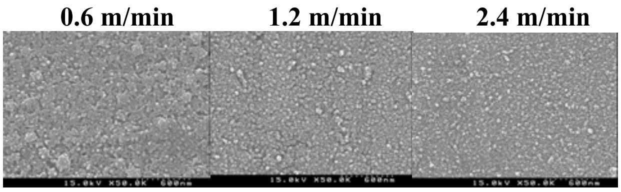

Fig. 8 SEM images of OPZ layer surfaces obtained at various line speeds.

Uniformity of contact angle and adhesion. In order to evaluate the uniformity of large scale OPZ system, the samples were taken at 5 positions with spacing of 125 mm in 600 mm wide Al roll sheet modified by OPZ. In Fig. 9, 0 indicate central position, and negative value goes toward left side from center. Difference of contact angles in lateral direction at fixed line speed was within maximum of 4°. The hydrophilic property of Al treated by continuous OPZ process is shown to be very uniform, laterally.

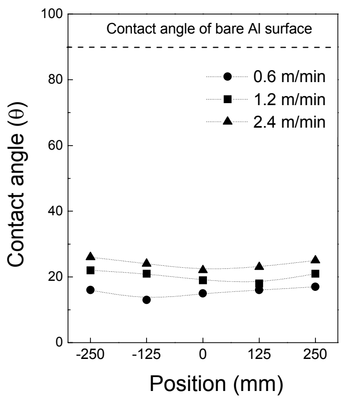

Fig. 9 Contact angle of Al treated by OPZ with position and line speed

As shown in Fig. 10, the layer surfaces obtained at different places represented the same morphology with homogeneous particle size. Uniformity of large area polymer coating by OPZ process is thought to be good in the point of view of morphology.

Al without any treatment has a very hydrophobic surface, which makes it difficult to improve its painting property. Paintability of Al surface could be improved by increasing wettability. Therefore, the uniformity in hydrophilic treatment of Al by OPZ was also identified by its adhesion performance with respect to paints.

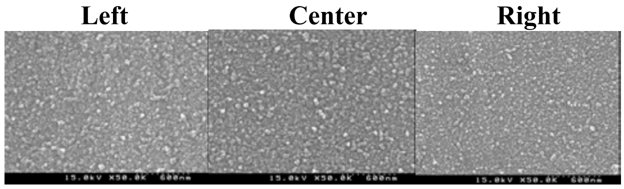

Fig. 10 SEM images of OPZ layer surfaces on different places at line speed of 2.4 m/min.

Fig. 11 shows results of tape peel test for paints on OPZ-treated Al for different places at line speed of 2.4 m/min. In the case of untreated Al surface, the painted area over 40% was peeled off, showing the poor adhesion property. However, all the samples taken at left, center, and right positions of Al roll sheet revealed good adhesion of paints to OPZ-treated Al, which means that the interfacial adhesion of OPZ-layer/Al as well as the hydrophilicity of OPZ layer would be excellent.

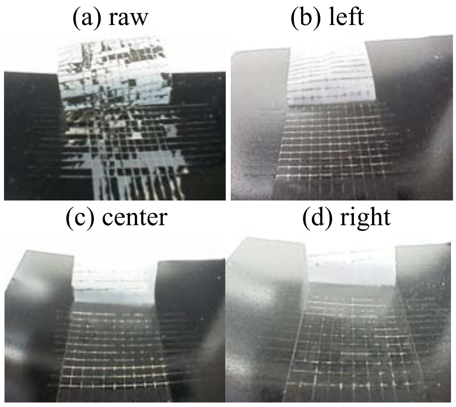

Fig. 11 Results of tape peel test for paints on OPZ treated Al at different places.

Durability of hydrophilicity. In order to investigate the long term durability of hydrophilic property of OPZ treated Al surface, the contact angles of OPZ treated Al were measured with storage time in water environment, and its results is shown in Fig. 12. In the case of surfactant coating in water environment, the hydrophilicity of layer is gradually lost with time due to the dissolution of surfactant in water. The surfactant coated Al reveals the good wettability at initial stage, but the surface of Al recovers to the hydrophobic surface of bare Al without any treatment in certain period of operation. However, it can be known from Fig. 12 that the hydrophilicity of OPZ treated Al surface maintains even after the storage time of 540 days in water environment, meaning that the hydrophilic groups on OPZ layer surface would be very stable, and could not be solved in water. So, OPZ treatment can overcome the problem in durability of hydrophilicity that occurs in the case of surfactant coating.

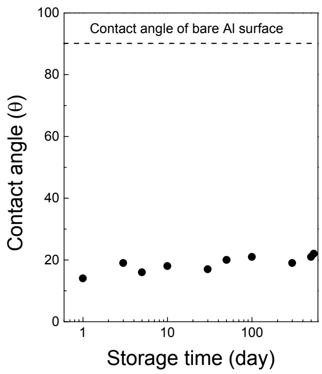

Fig. 12 Contact angle of OPZ treated Al surface as a function of storage time in water environment.

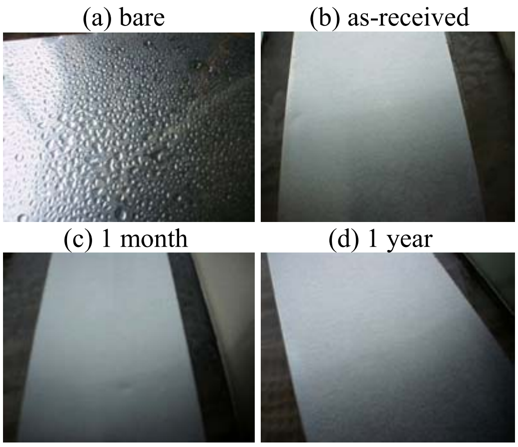

Fig. 13 Photographs of bare Al surface without any treatment (a) and OPZ treated Al surfaces after spraying water with storage time of as-received (b), 1 month (c), and 1 year (d).

In order to check visually the wettability of Al surface, the photographs of water sprayed OPZ treated Al surface with storage time in Fig. 12. On the surface of bare Al without any treatment, the sprayed water forms the droplet due to the hydrophobic surface. On the contrary, the sprayed water on OPZ treated Al surface exits in the form of film, resulting in entirely spreading out. As shown in Fig. 13(d), the Al treated by OPZ before 1 year reveals the good wettability as same as that of as-received sample. From these results, it is considered that the OPZ layer on Al possesses excellent long-term durability of hydrophilicity.

Residential Air-Conditioner using OPZ-Treated Al

Heat transfer performance. The heat exchanger for residential air-conditioner was produced with Al fin treated by large-scale continuous OPZ system. The heat transfer performance of heat exchanger with OPZ-Al fin was evaluated with the comparison of those with bare Al fin and surfactant coated Al fin. Fig. 14 shows heat transfer rate and fan power for heat exchangers with bare Al fin, surfactant coated Al fin, and OPZ treated Al fin. Here, fan power, FP, is calculated by equation (1).

$$FP = Q \times \bullet P \qquad (1)$$

At a fixed heat transfer rate, heat exchanger with OPZ treated Al requires the same fan power as that with surfactant coated Al within ± 5 %.

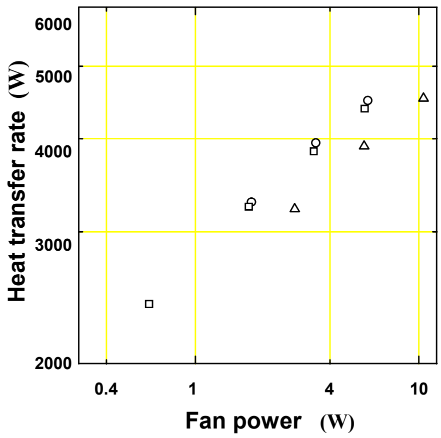

Fig. 14 Heat transfer performance of wet coil for bare Al without any treatment (•), surfactant coated Al (•), and OPZ treated Al (•).

However, heat exchanger with bare Al fin needs 56 % more fan power than that with Al of hydrophilic surface, resulting from higher pressure drop in heat exchanger with hydrophobic Al fin surface. In other words, when using Al fin of good hydrophilic surface, higher heat transfer rate could be obtained at a fixed fan power. If the wettability of fin surface were good, the condensate drainage of heat exchanger would be improved. This leads to higher air velocities for the same air pressure drop, and at fixed air velocity, good wettability of fin surface would result in reduced fan power and lower aerodynamic noise level. From these results, it is identified that the heat transfer performance could be improved by use of Al fin treated by OPZ.

Aging test. In the last section, heat exchanger with the surfactant coated Al fin showed the heat transfer performance as good as that with OPZ treated Al fin, compared with that with bare Al fin. The retention of heat transfer performance with operation is very important property in the real production. The long-term performance of heat exchangers with surfactant coated Al fin and OPZ treated Al fin with wet/dry cycle is shown in Fig. 15.

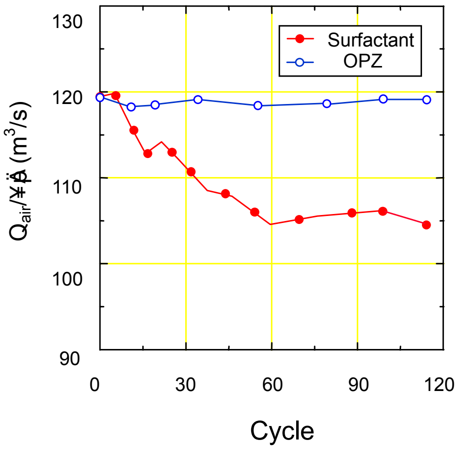

Fig. 15 Performance of heat exchangers with surfactant coated Al fin and OPZ treated Al fin at air frontal velocity of 1.5 m/s as a function of wet/dry cycle.

One wet/dry cycle includes one hour wet coil test and consecutively one hour dry coil test. During wet test of wet/dry cycle, the water moisture is condensed on fin surfaces of heat exchanger. At dry test of wet/dry cycle, the heat exchanger is dried by fan without water flow inside tube. As shown in Fig. 15, the performance of heat exchanger with surfactant coated Al fin was deteriorated with increase of cycle, while that with OPZ treated Al fin maintained its initial value, even after 110 wet/dry cycles. Surfactant has good hydrophilic property, but is soluble in water, resulting in loss of hydrophilicity in the long run. However, as identified in section of durability of hydrophilicity, the OPZ treated layer could not be dissolved in water, not like as surfactant, and have the characteristics of permanent hydrophilicity. Therefore, heat exchanger with OPZ treated Al exhibits no aging property in respect to the performance improved by wettability. In conclusion, the hydrophilic polymer layer was continuously coated on the Al sheet of large area by large scale OPZ system, and the use of OPZ treated Al fin for heat exchanger could enhance the performance of heat exchanger.

CONCLUSIONS

1. The contact angle of bare Al surface without any treatment is 90°, and the contact angle of Al surface modified by OPZ ranges from 42 to 23° as a function of nitrogen ratio in mixture gas. OPZ treatment can remarkably enhance the hydrophilicity of Al surface.
2. The hydrophilic groups on layer created by OPZ are –C-O-, -(C=O)-, -C=N-, and C-N bonds, confirmed by XPS analysis. These hydrophilic groups make the surface very wettable.
3. From the results of large scale OPZ system, it is known that the hydrophilicity of Al surface treated by OPZ is excellent irrespective of line speed and position. OPZ treated Al reveals the long-term durability of hydrophilicity.
4. In the heat exchanger for the residential air-conditioner, the use of OPZ treated Al fin can reduce the fan power at fixed heat transfer rate, resulting from the decrease of pressure drop due to the improved water drainage.
5. The improved heat transfer performance of OPZ treated Al fin could not be deteriorated with operation, opposite to that of surfactant coated Al fin.

NOMENCLATURE

•P Air side pressure drop, Pa
Q Air flow rate, m^3/s
Q_{air} Air side heat transfer rate, W

Subscripts

air : Air side

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