

# Surface Wettability Properties of 304 Stainless Steel Treated by Atmospheric-Pressure Plasma System

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## Abstract

The ability to control the wetting properties of stainless steels (SS) is extremely beneficial as a common metal in many areas of daily life as well as for scientific and industrial applications due the their corrosion resistance. Different kind of methods (physical and chemical treatments, plasma, laser treatments, mechanical surface modifications, various hydrophilic and hydrophobic coatings) have been employed to control the wetting properties of SS surface. Depending on the treatment used, the modification can be altered the surface properties of the SS. In this study the wetting properties of stainless steel (SS) plates treated with atmospheric pressure plasma (APP) using three different parameters (gap distance, nozzle scan velocity, pass number) were measured using the Laplace-Young contact-angle (CA) technique. According to the control parameter and surface contact angle measurement results we have succeeded to hydrophilic surfaces. All these plasma treatment parameters can contribute to an improvement of wettability and/or of adhesion properties of the surface.

Key words: Stainless Steel, Plasma Treatment, Surface Wetting Control, Contact Angle

# **1. Introduction**

Stainless steels (SS), which is iron based alloy with chromium content is resistant to corrosion and thermal stability, have been used wide range of application. This extensive usage of stainless steel is result of its high atmospheric/ thermal resistance and surface characteristic properties. Most commonly used stainless steel are austenitic 300 series (AISI 304, 316, 309, 310). Wettability properties of stainless steel have great interest for many industrial applications, where stainless steel-fluid contact occurs, such as petrochemical, power generation, marine, food, and construction industries. Thereby the control of wettability has great importance [1]–[4].

Wettability of the solid surface is a characteristic property of metals and largely depends on the chemical composition, surface energy and the surface structure. The wetting property of a solid surface is generally characterized by the contact angle ( $\Theta$ ) measurement, which is given by the wellknown Young's equation :  $\gamma_{SV} = \gamma_{SL} + \gamma_{LV} \cos(\Theta)$ , where,  $\gamma_{SV}$ ,  $\gamma_{SL}$  and  $\gamma_{LV}$  are the solid–vapor, solid–liquid and liquid–vapor interfacial energies per unit surface, respectively. A surface on which water contact angle is between 10° and 90°, commonly called a hydrophilic surface. This surface characteristics improve the adhesion of various paint and coatings [5]. And also,

wetting controllability has a wide range of applications including enhancement of adhesion improvement for surface coatings and self-cleaning and anti-icing surface fabrication. The ability to control the wetting properties of SS is extremely beneficial as a common metal in many areas of daily life as well as for scientific and industrial applications. Various existing methods have been employed to control the wetting properties of SS surfaces. These are: physical and chemical treatments, plasma treatments, laser surface modification, ion implantation, various hydrophilic and hydrophobic coatings. Among them the plasma surface treatments is highly effective and economical method for controlling surface properties [6], [7].

Plasma treatment has been an efficient method for modifying the surface properties of many materials and offers a possibility to create a surface with new functions. Nowadays, a great deal of research has been performed to improve the surface properties of polymers and metals by using plasma treatment. The atmospheric pressure air plasma is generated when air at atmospheric pressure and near ambient temperature is exposed to an electrical field. The chemical reactivity of the plasma takes place in non-equilibrium conditions, and the chemical reactions can take place while the gas or parts of it remain at relatively low temperatures. The plasma contains radicals, ions, photons and other excited species. These species can interact either physically or chemically with the substrate surface to a depth of a few tens of nm owing to their high reactivity. As a result of plasma treatment the surface may be oxidized (generating new chemical groups), and/or degraded as a result of the etching effect (removal of surface material), whereas the bulk properties remain intact. By varying the plasma parameters, such as the nature of the gas composition and its flow rate, the plasma power, nozzle type, standoff distance and the exposure time, a great variety of surface effects can be obtained [6]–[8].

APP provide plasma treatment for efficient surface modification of plastic, metal, textiles, glass and composite materials for produce hydrophobic or hydrophilic surface. Recently, APP was using pretreatment step for components will be coated, painted or improving their adhesion property. APP is non-pollution system, so it's important for producing environment friendly solution. In order to understand and control the wettability behavior of stainless steel, atmospheric-pressure plasma jet (APP) used for surface modifications. Thereby, in this study we modified the stainless steels surface to obtain optimum conditions for hydrophilic surface with APP system.

#### 2. Materials and Method

APP experiments are carried out using open air plasma system (Openair®) with rotary nozzle developed by Plasmatreat (Steinhagen, Germany). Fig. 1 shows rotary nozzles images. The plasma source was dried air, plasma parameters were 280V / 16A, 21Hz and 4 bar air. The jet nozzle body is fixed on the frame of the X–Y-Z moving table equip with benchtops robot Janome JR2300N.

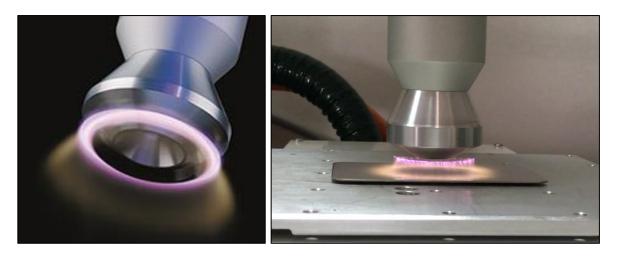


Figure 1. Rotary Plasma Nozzle İmages [9].

Atmospheric-pressure plasma jet used in different control parameters such as velocity, gap distance and the number of passes which means repeating the APP proses multiple times. AISI 304 stainless steel used for this experiments were 10mm x 5mm x 0,5mm thick, Table 1 shows its standard composition. Before plasma treatment, the stainless steel samples surface are cleaned in acetone, methyl alcohol, and de-ionized water by ultrasonic cleaning method. All the treatments carried out under the room temperatures. Surface wettability tests were performed on irradiated and microstructured AISI 304 SS sample surfaces with 4  $\mu$ L deionized (DI) water droplets, and static contact angles were measured with Krüss drop shape analyzer, and average contact angle determinate after three measurements. Also we perform aging test, it's important to know how long the effect stand on the surface for industry applications.

Component	Wt. %
С	Max 0,08
Cr	18-20
Fe	66,345-74
Mn	Max 2
Ni	8 - 10,5
Р	Max 0,045
S	Max 0,03
Si	Max 1

Table 1. AISI Type 304 Stainless Steel Composition

# 3. Results and Discussion

To start with, we performed contact angle analysis to control wettability properties of stainless steel. Fig. 2 show before and after treatment contact angle images of 304 stainless steel. Plasma's effect is change with two important key factor, first one is gap distance between plasma distance and the surface and the other one is treatment time per unit area of the surface. Gap distance and velocity can be control precisely with benchtop robot. After cleaning the surface of stainless

steel, non-treated (NT) samples contact angle measured 74,18°, this value compared with plasma threated samples contact angles.

#### 3.1. Distance effect on contact angle

Plasma treatment process applied on stainless steel in two different gap distance with constant parameters. Fig. 2 shows gap distance and velocity effect on contact angle. Efficiency of plasma treatment change with gap distance between nozzle mouth and sample surface. In literature, plasma treatment process could be applied with different gap distance depend on nozzle type and sample geometry. In our experimental studies, we determine gap distance as an 8mm and 13mm, this values determined with the help of previous studies. In previous studies it's found that under 6mm and above 15mm the plasma-surface interaction is poor. Stainless steel surfaces contact angle measured with 8mm and 13mm gap distance in fixed 25mm/s velocity, thus in 8mm gap distance contact angle measured 34,01°, on the other hand in 13mm gap distance contact angle measured 74,18° to 34,01°. Its concluded that 8mm gap distance have better wettability yield than 13mm gap distance at fixed 25mm/s velocity.

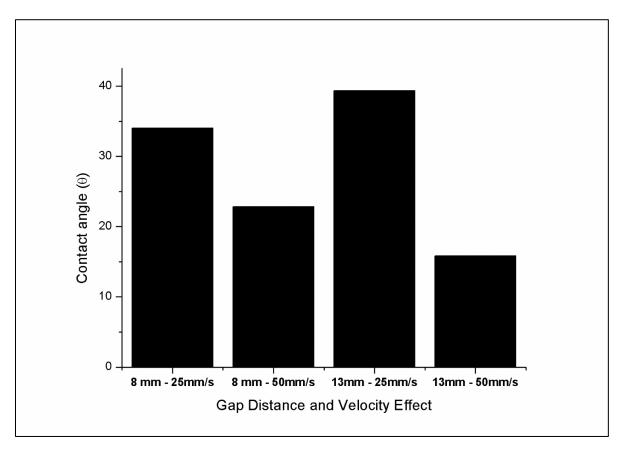


Figure 2. Gap distance and velocity effect on contact angle

Plasma treatment process applied on stainless steel in two different gap distance with constant parameters. Plasma treatment's sweep rate of the surface defined the plasma treatment time per unit area on the surface. This time is very important for the plasma's efficiency. 25mm/s and 50mm/s velocities resulted with different contact angle measurements. As can be seen Fig. 2 contact angle degraded 34,01° to 22,84° with increasing to plasma treatment velocity 25mm/s to 50mm/s in 8mm gap distance. As for 13mm gap distance, contact angle degraded 39,37° to 15,82° with increasing to plasma treatment velocity 25mm/s to 50mm/s. In both cases it's concluded that increasing velocity caused decreasing to contact angle.

The evidence from these studies in fixed plasma parameters, gap distance and velocity could be effect of wettability properties of stainless steel as you can see abovementioned results. Thereby, in fixed velocity at 25mm/s, contact angle increased 34,01° to 39,37° with increasing of gap distance (8mm to 13mm), on the other hand in 50mm/s velocity, contact angle decreased 22,84° to 15,82° with increasing of gap distance. This has revealed two different results. After that, the examination ascertain that substrate reach different temperature depending on plasma velocity and gap distance, hence this change effect wettability behavior of stainless steel.

As shown Table 2. surface temperature of stainless steel decreased with increasing velocity of plasma treatment. Hence the temperature increased +4 centigrade ( $40,7^{\circ}C$  to  $44^{\circ}C$ ) with increasing gap distance 8mm to 13mm in 25mm/s plasma velocity. On the other hand, in 50mm/s plasma velocity have no significant effect on the surface temperature, whereas temperature rise on surface of the stainless steel play significant role on contact angle change at low velocity.

Gap distance	8 mm	8 mm	13 mm	13 mm
Velocity	25 mm/s	50 mm/s	25 mm/s	50 mm/s
1 Pass	40,7°C	38°C	44°C	37°C
4 Pass	62°C	48,9°C	56,8°C	51°C

**Table 2.** Temperature changes with gap distance and velocity.

#### 3.3. Pass effect on contact angle

Contact angle shows a decreasing tendency on stainless steel with multiple plasma treatment as shown in Fig. 3 number of passes (1 to 4) effect on stainless steel. Fig. 4 shows contact angle images taken with drop shape analyzer.

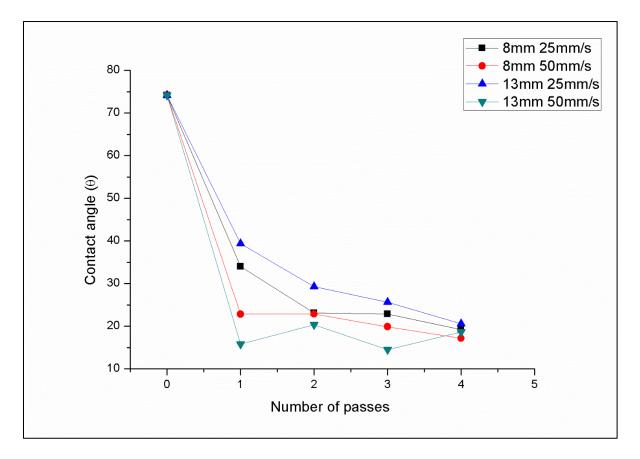
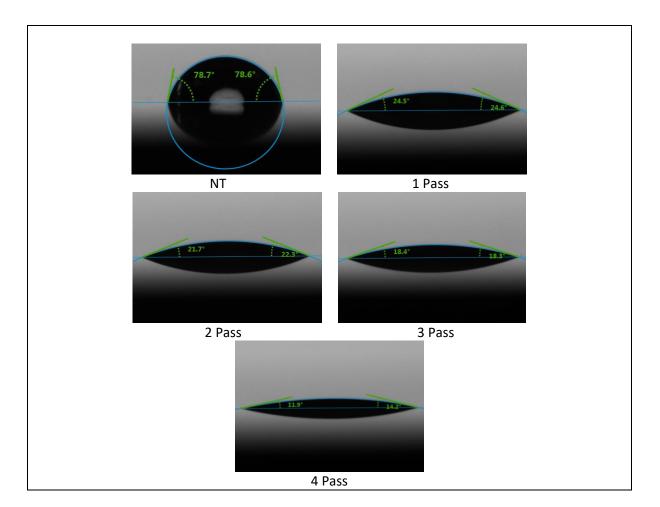


Figure 3. The effect of number of passes on contact angle

Table 3 shows contact angles changes with number of passes. The most contact angle decrease happened 1 plasma treatment with 13mm gap distance at 50mm/s velocity. Non-treated beginning contacts angle of stainless steel which is 75° decreased 40° level with one sweep of plasma treatment than its reach 20° level with four sweep of plasma treatment on the same area. The contact angles values were close together with increased number of passes the plasma. Substrate temperature is changed with number of passes and this is also effect contact angle results. Substrate temperature increased  $38\pm4$  to  $55\pm4$  with increased number of passes (1 to 4). Most temperature increased on substrate surface happened with 8mm gap distance at 25mm/s velocity, on the other hand surface temperature stayed still 50°C level with 50mm/s velocity without depending on gap distance. It's concluded that substrate temperature above 50°C, wettability properties of stainless steel couldn't control with plasma treatment.





Gap distance	8 mm	8 mm	13 mm	13 mm
Velocity	25 mm/s	50 mm/s	25 mm/s	50 mm/s
NT	74,18	74,18	74,18	74,18
1 Pass	34,01	22,84	39,37	15,82
2 Pass	23,14	22,87	29,3	20,33
3 Pass	22,89	19,91	25,66	14,52
4 Pass	19,19	17,2	23,66	18,67

 Table 3. Contact angles change

# 3.4. Aging effect

Atmospheric pressure plasma application (fixed 50mm/s velocity and 4 pass) effect on contact angle change with time on stainless steel surface shown Fig. 5. In both gap distance contact angle rises 20° to 30° level after 45 minutes. After 150 minutes, contact angle rise 40° level on 8mm gap distance whereas contact angle stayed close angles on 13mm gap distance. This situation explain that plasma treatment has more stable effect with more time on stainless steel with 13mm gap distance.

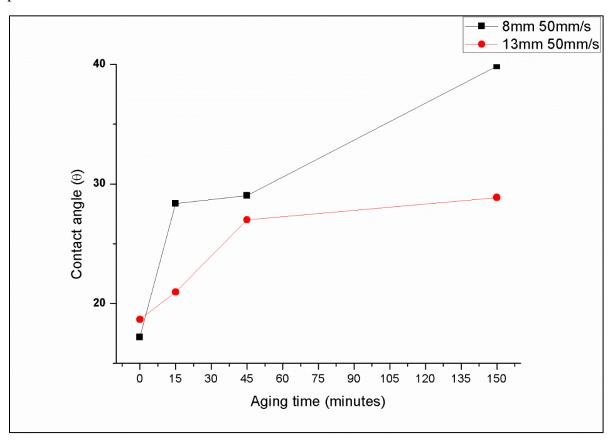


Figure 5. Contact angle data obtained with different expose time of plasma treatment.

## 4. Conclusion

Surface wettability properties of stainless steel surface chanced with different gap distance, velocity and multiple passes with atmospheric pressure plasma treatment, contact angle decreased  $75^{\circ}$  to  $20^{\circ}$  level. Lowest contact angle (16±2) obtained on 13mm gap distance at 50mm/s velocity at 1 pass with surface activation via plasma treatment. Multiple sweeps does not have significant importance on contact angle because of its cause rising the temperature of the surface. Plasma effect more stable with time when substrate temperature below 50°C temperatures. It is foreseen that APP process increase the ability of paint adhesion, coatability on the stainless steel surface.

#### Acknowlodgements

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# References

- [1] H. S. Khatak and B. Raj, *Corrosion of Austenitic Stainless Steels*. Woodhead Publishing, 2002.
- [2] S. Tang, O.-J. Kwon, N. Lu, and H.-S. Choi, "Surface free energy changes of stainless steel after one atmospheric pressure plasma treatment," *Korean J. Chem. Eng.*, vol. 21, no. 6, pp. 1218–1223, Dec. 2004.
- [3] M. C. Kim, D. K. Song, H. S. Shin, S.-H. Baeg, G. S. Kim, J.-H. Boo, J. G. Han, and S. H. Yang, "Surface modification for hydrophilic property of stainless steel treated by atmospheric-pressure plasma jet," *Surf. Coatings Technol.*, vol. 171, no. 1–3, pp. 312–316, Jul. 2003.
- [4] M. C. Kim, S. H. Yang, J.-H. Boo, and J. G. Han, "Surface treatment of metals using an atmospheric pressure plasma jet and their surface characteristics," *Surf. Coatings Technol.*, vol. 174–175, pp. 839–844, Sep. 2003.
- [5] Y. Yuan and T. R. Lee, "Contact Angle and Wetting Properties," in *Surface Science Techniques*, 2013, pp. 3–34.
- [6] L. J. Chen, M. Chen, H. Di Zhou, and J. M. Chen, "Preparation of super-hydrophobic surface on stainless steel," *Appl. Surf. Sci.*, vol. 255, no. 5, pp. 3459–3462, Dec. 2008.
- [7] D. H. Kam, S. Bhattacharya, and J. Mazumder, "Control of the wetting properties of an AISI 316L stainless steel surface by femtosecond laser-induced surface modification," J. *Micromechanics Microengineering*, vol. 22, no. 10, p. 105019, Oct. 2012.
- [8] J. Toshifuji, T. Katsumata, H. Takikawa, T. Sakakibara, and I. Shimizu, "Cold arc-plasma jet under atmospheric pressure for surface modification," *Surf. Coatings Technol.*, vol. 171, no. 1–3, pp. 302–306, Jul. 2003.
- [9] "http://www.plasmatreat.com/.".