Surface modification of SUS304 stainless steel by atmospheric pressure
Ar/N₂/O₂ plasma

Jau-Wen Lin*, Hsi-Cherng Chang

Department of Mechanical Engineering, National Kaohsiung University of Applied Sciences, 415 Chien-Kang Road, Kaohsiung City 807, Taiwan

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The surface characteristics of SUS304 stainless steel are investigated before and after surface modification by Ar/N₂/O₂ plasma under atmospheric pressure conditions. It was found that plasma treatment of a stainless steel plate has a significant effect on the wettability, contact angle, and free energy of the SUS304 surface. The contact angle and surface free energy were analyzed. The optimal surface modification parameters are a power of 1000 W, a torch-to-sample distance of 80 mm, a treatment time of 300 s, and an oxygen content of 1.5 wt%. Under these processing conditions, a contact angle of just 1.60° was obtained. The surface morphology, surface element composition, and surface roughness of the treated SUS304 specimens were examined using scanning electron microscopy (SEM), and atomic force microscopy (AFM), respectively. The results show that the optimal surface modification conditions lead to the formation of fine, uniformly distributed crystallites in the SUS304 microstructure. Moreover, compared to the untreated surface, the treated surface had a significantly lower carbon content and a more uniform distribution of surface peaks.

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1. Introduction

SUS304 stainless steel is widely used in the fabrication of items such as medical instruments, petrochemical components, and ship parts, due to its favorable mechanical, chemical, thermal, and magnetic properties. However, its low hardness and deficient wear resistance limit its application in many fields [1,2]. Most industrial applications that require surface adhesive strength, e.g., machinery tools, rely on the surface characteristics of the materials involved. To increase surface adhesion without affecting the overall mechanical properties of the material, surface modification is generally implemented in the near-surface range. The surface modification of stainless steel prior to application is a critical process and is important to surface coating. Many investigations have been conducted on the surface modification of a wide variety of organic materials, inorganic materials, and metals [3–10]. Plasma treatment is one of the most commonly used surface modification methods due to its favorable wettability, permeability, conductivity, adhesion, and biocompatibility properties [3].

Tang et al. [11] utilized atmospheric plasma to modify the surface characteristics of AISI 304L at room temperature. The results showed that the plasma treatment increased both the wettability and the free energy of the AISI 304L surface. Shin et al. [12] improved the adhesive properties of surface paint coatings on metal surfaces by modifying the surface using Ar gas at atmospheric pressure. Kim et al. [13] used an atmospheric-pressure plasma jet to modify aluminum, stainless steel, and copper surfaces, and then examined the resulting surface activation properties by measuring the corresponding contact angles. Kwon et al. [14] enhanced the surface hydrophobicity of polypropylene (PP) using an Ar/O₂ mixture as the reactive gas. The results showed that the free energy of the modified surface increased with increasing oxygen content in the reactive gas. Kim et al. [15] used N₂/O₂ plasma to modify the surface properties of stainless steel at room temperature. The change in the hydrophilicity of the surface was then evaluated by measuring the contact angle. Lee et al. [16] modified the surface properties of cold-rolled steel using Ar/O₂ plasma, and showed that the surface adhesion improved with increasing oxygen content.

The present study investigates the surface characteristics of SUS304 stainless steel before and after surface modification using Ar/N₂/O₂ plasma under atmospheric pressure conditions. The effects of the treatment parameters (i.e., power, torch-to-sample distance, treatment time, and oxygen content) on the wettability, contact angle, and free energy of the SUS304 surface were systematically examined in order to determine the optimal treatment conditions. The morphology, surface element composition, and surface roughness of the various SUS304 specimens were examined using scanning electron microscopy (SEM), and atomic force microscopy (AFM), respectively.
2. Experiment details

2.1. Specimen preparation

Stainless steel plates with dimensions of 10 × 10 × 2 mm were prepared using a laser cutter. The plates were ground progressively using 240, 400, 600, 1000, and 1200 grit abrasive paper. The ground plates were then polished to a mirror-like finish using a 0.5-μm Al₂O₃ slurry. The polished plates were immersed in acetone and cleaned ultrasonically for 10 min in order to remove any traces of oil or other contaminants from the surface. Finally, the plates were blown in nitrogen gas to remove residual water and then set aside to dry.

2.2. Experimental equipment: Microwave plasma torch

Fig. 1 shows a schematic illustration of the microwave plasma torch system used in the present study. The major components include a gas inlet system, a microwave power supply, a microwave generator, a waveguide, and a cooling system. In the surface treatment process, microwaves were produced by driving the magnetron in the microwave generator using a high-voltage power supply. The microwaves were coupled into a waveguide and then fed to a resonator located within a reactor chamber, resulting in the formation of a fluctuating magnetic field with a frequency of approximately 2.45 GHz. The reactive gases were mixed in the appropriate ratio and introduced into the reactor chamber. The fluctuating electric field transformed the reactive gases into plasma, which was then output through a torch located a short distance above the sample surface. Since the surface treatment process was performed under atmospheric pressure conditions, a lot of heat was generated in the reactor chamber and waveguide. Consequently, a liquid-based cooling system was employed to cool the critical system components. Both the MW(Microwave) and the previously mentioned high-frequency system used a quartz or ceramic tube as the reactor chamber. In addition, both systems were equipped with electrode-less discharge and required an external device to ignite the plasma (also known as ignition).

2.3. Surface modification by atmospheric plasma

2.3.1. Surface modification at various values of power, treat time, torch-to-sample distance, and resonance distance

In the first set of experiments, the surface treatment process was performed using a mixture of Ar and N₂ as the reactive gas. Using a mass flow controller (MFC), the reactive gas ratio was set as follows: N gas: 9 slm, Ar gas: 1 slm, and N₂ gas: 2 slm, for a total gas flow rate of 12 slm. To determine the optimal processing conditions, the surface treatment experiments were performed using various values of power, torch-to-sample distance, and treatment time, as shown in Table 1, where “power” denotes the power supplied to the microwave generator and “distance” denotes the distance from the torch to the sample surface.

2.3.2. Surface modification with various ratios of oxygen content

In the second series of experiments, the surface treatment process was performed using the same set of processing conditions shown in Table 1, but with oxygen added to the Ar/N₂ reactive gas mixture in ratios of 0.5, 1.0, 1.5, 2.0, and 2.5 wt%, respectively.
philicity and the surface energy are reduced following exposure to the atmosphere. Fig. 7 shows the variation of the contact angle with aging time in air. It can be seen that the contact angle increased by a factor of approximately three (i.e., from 7.1° to 20.63°) following aging for 10 min. Moreover, the contact angle increased to 61.86° after 30 min and 78.88° after 60 min. Following aging for 1440 min (1 day), the contact angle reached 81.75°. Although the contact angle increased continuously with increasing aging time, the results show that the contact angle increased most rapidly during the early stages of aging (i.e., <60 min). These results are consistent with those reported in a study by Tang et al. [11], where prolonged aging in air was found to have an adverse effect on the condition of the treated substrate; i.e., during the initial phase of exposure to air, the increase in contact angle was the largest. This increase gradually slowed with time.

3.2. Scanning electron microscopy (SEM) and atomic force microscopy (AFM) results

The morphology and elemental composition of the SUS304 stainless steel substrates were examined before and after surface modification using SEM and AFM, respectively.

3.2.1. SEM analysis

Fig. 8 compares the surface morphology of an untreated SUS304 substrate with that of substrates treated using Ar/N2 plasma under conditions of 800 W/60 mm/180 s and 1000 W/80 mm/90 s, respectively. Fig. 8a shows that the surface of the untreated substrate has a relatively rough appearance, as shown in Table 2. However, following plasma treatment, oxides and nitrides formed on the surface, and thus the surface became more even. The surface morphologies shown in Fig. 8b (treatment time of 180 s) and c (treatment time of 90 s) have a similar appearance. The similarity in the morphologies of the two samples confirms that a higher treatment power accelerates the surface modification effect.

Fig. 9a and b show the surface morphologies of SUS304 substrates treated under conditions of 1200 W/60 mm/180 s and 1000 W/80 mm/300 s, respectively. Both surfaces contain evenly distributed crystallites and have similar quantities of oxides. However, the contact angle of the substrate shown in Fig. 9a is 7.55°, whereas that of the substrate shown in Fig. 9b is 7.1°. In other words, the results once again confirm that the use of a higher treatment power yields a more rapid surface modification effect.

Fig. 10a and b show the surface morphologies of SUS304 substrates treated using Ar/N2/O2 plasma under conditions of 1000 W/80 mm/300 s/1.5 wt% and Ar/N2 plasma under conditions of 1000 W/80 mm/300 s/1.5 wt%, respectively. It can be seen that the surface morphology of the sample treated using Ar/N2/O2 plasma contains smaller and more evenly distributed crystallites than those of the sample treated using Ar/N2 plasma. In other words, the addition of oxygen to the reactive gas has a refining effect on the morphology of the treated surface.

3.2.2. AFM analysis

The morphologies and roughness properties of plasma-treated surfaces are directly related to the chemical and physical reactions which take place during the treatment process. The chemical reactions are induced by the generation of substances such as oxides and nitrides on the substrate surface, and the physical reactions originate from the etching and bombardment effects of the high-energy particles in the plasma. Kim et al. [13] reported that under certain conditions, plasma treatment results in the formation of aligned crystallite structures on the modified surface. Furthermore, it was shown that while the original substrate had an uneven surface with peaks of various heights, the modified substrate had a more even surface with low peaks.

In the present study, the surface roughness characteristics of the treated SUS304 samples were investigated using AFM. Fig. 11 shows the AFM surface morphologies of the untreated SUS304 substrate (Fig. 11a), the substrate treated with Ar/N2 plasma under conditions of 1000 W/80 mm/300 s (Fig. 11b), and the substrate treated with Ar/N2/O2 plasma under conditions of 1000 W/80 mm/300 s/ 1.5 wt% (Fig. 11c). From inspection, the average surface roughness of the untreated substrate is approximately 174.62 nm. Fig. 11a shows that the surface contains various peaks of widely varying heights. Moreover, it can be observed that the peaks are clustered within certain limited areas of the surface. Following treatment with Ar/N2 plasma, the substrate had a reduced surface roughness (~128.49 nm) and a more uniform distribution of the surface peaks (see Fig. 11b). In the Ar/N2/O2 treatment process, the oxygen particles and oxygen-containing groups in the plasma react spontaneously with the surface and result in the production of oxides and fine crystallite structures. As shown in Fig. 11c, the surface peaks were uniformly distributed. Moreover, from inspection, the average surface roughness is around 168.66 nm.

4. Conclusion

This study investigated the surface characteristics of SUS304 stainless steel specimens before and after surface modification by Ar/N2/O2 plasma under atmospheric pressure conditions. The experimental results support the following major conclusions.

1. The surface contact angle significantly decreased following a treatment time of 10 s, indicating a significant improvement in the hydrophilicity of the surface.
2. The optimal surface modification parameters are a power of 1000 W, a torch-to-sample distance of 80 mm, a treatment time of 300 s, and an oxygen content of 1.5 wt%. Under these processing conditions, a contact angle of just 1.60° was obtained.
3. Ar/N2/O2 plasma yields a lower contact angle than that obtained for Ar/N2 plasma under the optimal treatment conditions (1.60° vs. 7.1°). Moreover, the crystallites that formed on the surface modified using Ar/N2/O2 are finer than those formed on the surface modified using Ar/N2.
4. The oxygen content of the modified surface increased from around 0.71% to approximately 11.3% irrespective of the plasma used. However, the carbon content of the surface modified using Ar/N2/O2 was significantly lower than that of the surface modified using Ar/N2 (0.61 vs. 2.05 wt%). For both plasma treatments, the modified surface had a more uniform distribution of the surface peaks than that of the unmodified surface.

References