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Surface treatment of metals using an atmospheric pressure plasma jet and their surface characteristics

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Abstract

We have treated the surfaces of Al, SUS and Cu metals using an atmospheric-pressure plasma jet generated by nitrogen and oxygen gases under the atmospheric pressure at room temperature. The plasma ignition occurred by flowing mixed gases between two coaxial metal electrodes, and the voltage was applied with impulse type and 16–20 kHz frequencies. The treated surfaces were basically characterized by means of a contact angle analyzer for the activation property on their surfaces. From the results of XPS, FE-SEM, OES and AFM, we could confirm that the main phenomena such as the reactive etching and oxidation were observed on their surfaces as well as even the aggregation of particles by the activated atoms, radicals and metastable species in the plasma space. However, all treated surfaces contained only oxygen and carbon without nitrogen, even though the excited nitrogen species were generated in the plasma due to its higher reactivity than oxygen ones observed in the OES data. The aging effect on the duration time of the surface energy, moreover, was also studied because of the production cost on the industrial applications in addition.

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1. Introduction

Recently, new surface treatments using non-isothermal low-temperature plasma are a subject of great interest. Plasma-chemical methods suitable for coating and surface treatment replace conventional galvanic methods since they are not as harmful for the environment as the classical ones. Many types of low-pressure plasma-chemical systems have been developed up to now, but most of them worked at low pressures in the range of several tens Torr or less. Practically all these systems require high-vacuum equipment whose cost is growing with dimensions of the technological process [1,2].

Plasma treatment for cleaning of the contaminants and surface modifications are, moreover, used in various applications to produce the new functional surfaces using metals, plastics, glass or polymers because thermally sensitive substrates can be used for treating. Plasma pre-treated metal products have new applications

in the field of automobile, printed circuit board (PCB) manufacturing, and electromagnetic interference (EMI) shielding materials, etc. which affects environmental non-pollution. This indicates that for these applications, the surfaces must be cleaned and activated resulting in enhancing the adhesion properties between metal–metal and metal–polymer interfaces [3,4].

In this study, therefore, we report the investigations of surface modification phenomena of different metal-surfaces by atmospheric plasma jet treated under the condition of nearly atmospheric pressure. The aims of our study are to obtain the optimum conditions with high surface energy and to understand the surface phenomena for increasing the adhesion property.

2. Experiment

Surface modification was carried out using the atmospheric-pressure plasma jet made by AgrodynTM. The power for the plasma generation and the sustenance were supplied with a voltage of an impulse type into the jet-nozzle electrode via a transformer. The maximum voltage and output frequency were approximately 10 kV

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from peak to peak and 16–20 kHz, respectively. The length of plasma jet flame was approximately 30 mm and the diameter was 10 mm, approximately. Mixed gases of N_2 and O_2 with ultra-high purity (99.999%) were used as the reactive gases with the ratios of $N_2/O_2=4:1$, (similar composition as air) and $N_2/O_2=1:4$ under nearly atmospheric pressure. The gases were manually controlled by flow-controllers and flowed constantly into the jet-nozzle for the plasma ignition. The substrates were sequentially cleaned in an acetone, methyl alcohol, and de-ionized water by an ultrasonic cleaning method. Al, SUS and Cu were used for surface modification as the substrates. For more clear recognition by AFM analysis, moreover, silicon (100) wafers that have more flat surfaces than those of metals were also cleaned by the same method and treated in the plasma space under the same conditions. All treatments were carried out at room temperature and continuously performed under the conditions with the relative humidity of 64% for 8 days for the aging tests.

In order to confirm the chemical and physical reactions on the metal surfaces, X-ray photoelectron spectroscopy (XPS), field emission scanning electron microscopy (FE-SEM), and atomic force microscopy (AFM) methods were used before and after surface modification. For investigation of the plasma jet contained the chemical activated species in the plasma space, optical emission spectroscopy (OES) was also used as optical diagnostic. The surface activities were, moreover, analyzed by contact angle analyzer, which was also adopted in the analysis of aging characteristics in sequence.

3. Results and discussion

3.1. Contact angle analysis

As the first step in our analysis, we carried out the contact angle measurements to obtain the optimum conditions, resulting in changing to the high surface energy as the parameters of nozzle-surface gap and nozzle moving velocity. Fig. 1a,b show the contact angle data of the plasma treated metal surfaces with the ratio of $N_2/O_2=4:1$, which is similar to a normal air. While the contact angles of untreated Al, SUS and Cu were 66.14, 49.92° and 64.72°, all obtained values from the plasma treated surfaces were largely decreased to the lowest values of 19.60, 10.92 and 23.20°, respectively. Furthermore, with increasing the nozzle moving velocity (1a) and nozzle-surface distance (1b), the contact angles were more increased due to reductions of the plasma density and heat. The combined results indicated that the plasma flames had relatively different concentrations of atoms and radicals, and the treating times affected the degree of surface activation and reactions. The

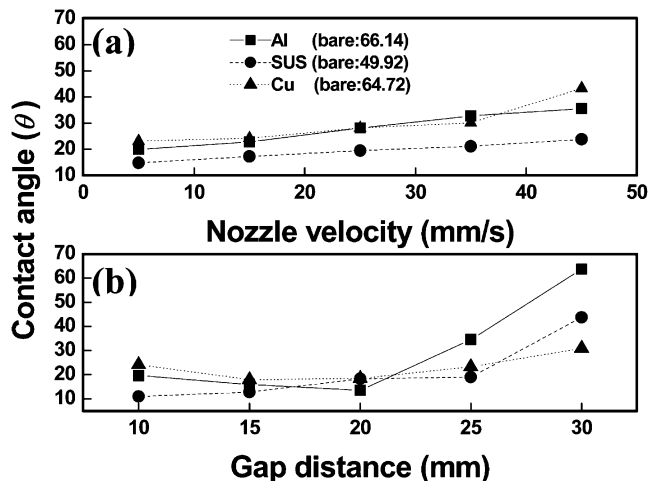


Fig. 1. Contact angle data under the different nozzle moving velocity (a) and nozzle to surface distance (b).

decreases of contact angles may be attributed to increase the total surface energy by cleaning and removing contaminants as well as a surface oxidation. Under these optimum conditions with the lowest contact angles, all the substrates were treated and analyzed in our experiments.

3.2. X-ray photoelectron spectroscopy (XPS) analysis

In the optimum conditions obtained from the contact angle data as mentioned above, Al, SUS and Cu substrates were treated using the mixed gases of $N_2/O_2=4:1$. To compare the surface modification phenomena between untreated surfaces and plasma treated ones, XPS study showing their survey spectra Fig. 2 was first carried out. All survey spectra clearly show the differences of photoelectron peaks of O 1s and 2p of metals as well as the O (KVV) Auger signals. Besides these relevant peaks, there also appeared the C 1s photoelectron peak and C (KVV) Auger signals for all the surfaces. It was considered that the carbon was mainly caused by both an impurity contained in the metal substrates and the air contamination such as CO_2 and CO molecules, which could be broken to pieces or excited to metastable states by plasma heat and collisions in the plasma jet processes. The other reason was that the carbon could be generated from the nozzle due to arcing with the nozzle materials at the hollow cathode plasma-jet system. In these results, the oxygen and carbon amounts, as atomic percent shown in Table 1, were larger and smaller than those of untreated surfaces, respectively. Therefore, it was identified as the effects of surface oxidation and reactive etching by highly activated species. Under the present results, the point of observation was that the nitrogen elements with the

types of atoms and chemical compounds have not appeared on the treated surfaces at all. From the face, it could be expected that the highly activated species generated from the nitrogen in the plasma space had not participated in chemical reactions as the surface adsorption but concerned with only a reaction in the gas phase and a reactive etching, mainly.

Fig. 3 shows the high-resolution XP spectra of O 1s and Cu 2p core-levels obtained from the plasma treated Cu substrate to characterize the chemical bonding states on the surface [5]. The observed oxygen peak in Fig. 3a analyzed from the untreated sample was originated from CO₂ and H₂O molecules adsorbed only on the surface in an air condition. After plasma treating, the new chemical bonding state was observed at approximately $E_b = 530.4$ eV, indicating the binding energy of the O–Cu, while the O 1s peaks caused by CO₂ and H₂O were reduced at the same time compared with the data of untreated ones. From the peaks of Cu 2p in figure (b), we could identify the same results as O 1s. It was important that the real chemical bonding between metal and oxygen were formed and oxygen particles, as grains, could be aggregated on the surface. These results could also be explained by surface morphology characteristics by means of AFM and FE-SEM analysis.

Table 1

Surface compositions of plasma treated surfaces by XPS analysis

At.%	C	O	Al	Si
Untreated Al	41.5	42.4	13.4	2.7
Treated Al	17.9	62.0	16.3	3.8
At.%	C	O	Fe	Cr
Untreated SUS	41.6	47.8	4.5	6.1
Treated SUS	24.7	59.3	16	0
At.%	C	O	Cu	Si
Untreated Cu	65.5	24.6	1.4	8.4
Treated Cu	36.1	45.8	18.1	0

3.3. Surface morphology characterizations by FE-SEM and AFM analysis

Fig. 4 shows the surface morphologies of Al metals obtained without plasma treatment (a) and with plasma treatment (b) under the ratio of N₂/O₂=4:1. From these figures, we could recognize that the new small particles were aggregated with a ball shape after plasma treating. To investigate the effect of mixed gas ratio, we have also treated the same samples under the condition of N₂/O₂=1:4 and the results are shown in Fig. 4c. In Fig. 4c, the new particle aggregations were increased

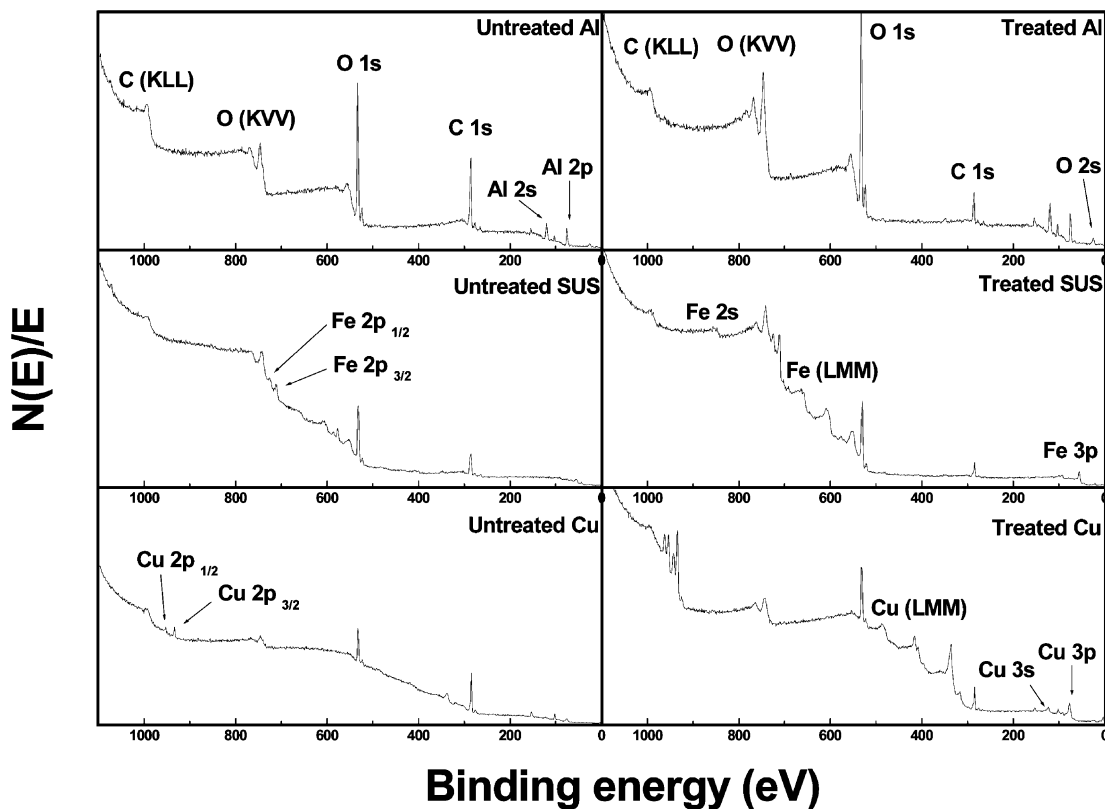


Fig. 2. XPS survey spectra of untreated and plasma treated Al, SUS and Cu substrates under the condition of N₂/O₂=4:1.

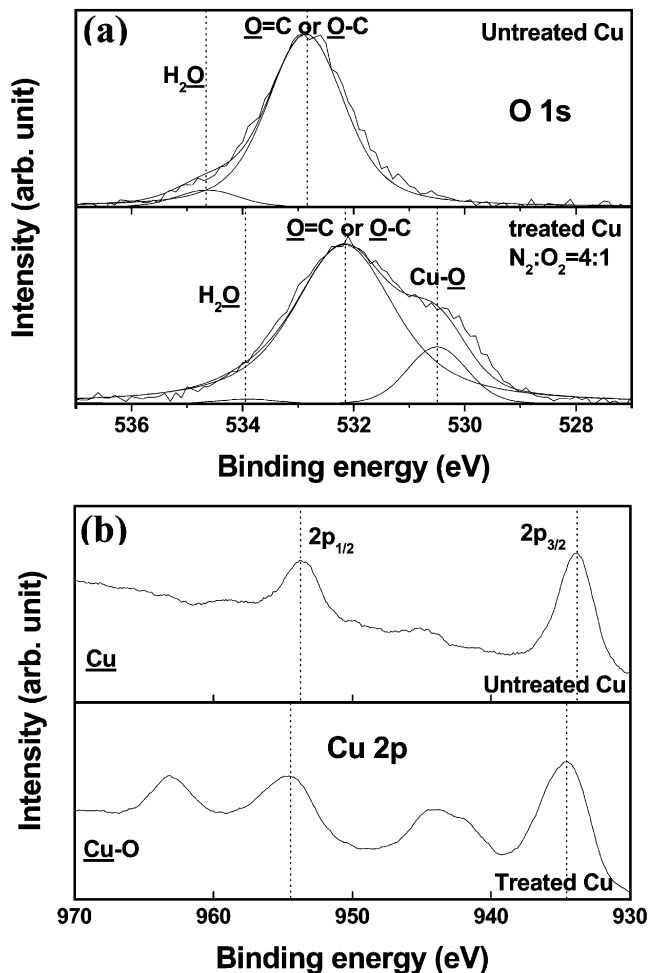


Fig. 3. O 1s (a) and Cu 2p core-level high-resolution XPS spectra of plasma-treated the same surface as Fig. 1b.

with increasing the oxygen rate and with decreasing the nitrogen amount, relatively. To confirm our FE-SEM results more clearly, we used Si (100) wafers for AFM analysis. Under the same conditions as metal substrates, we treated the Si (100) samples. Fig. 4d,e shows the results from $N_2/O_2=4:1$ (d) and $N_2/O_2=1:4$ (e). These figures clearly revealed that the Al and silicon surfaces were mainly bombarded and etched by the activated and excited atoms, radicals and metastable molecules containing the nitrogen in the condition of $N_2/O_2=4:1$. On the other hand, partially, it was expected that the particles consisted of metal, carbon, hydrogen from H_2O , and oxygen were aggregated on the metal surfaces at the same time in the condition of $N_2/O_2=1:4$. In this respect, the obtained results were corresponded to interpretation of XPS data. One of the aggregated particles with the shape of a ball in Fig. 4c was enlarged in Fig. 4f by means of FE-SEM analysis.

3.4. Optical emission spectroscopy (OES) analysis

We carried out the optical emission analysis to observe the electronically excited species generated by

N_2 and O_2 plasma jets. In Fig. 5, the emission spectra of the discharge at plasma flame were shown. In our OES observation, we found that the reactive and activated species, such as O^+ , O_2^+ , N_2^+ , N_2^{2+} , NO^- , OH^- and CN^- caused by arcing at nozzle, played an important role in reactive etching and particle aggregations [6–8]. By measuring the intensity of the spectral lines, it was possible to identify the densities of the excited states. One of the notable features in these spectra was the different intensity including the plasma density and activation. It could be explained by collision cross-sections between N_2 (0.43 nm^2) and O_2 (0.40 nm^2) [9].

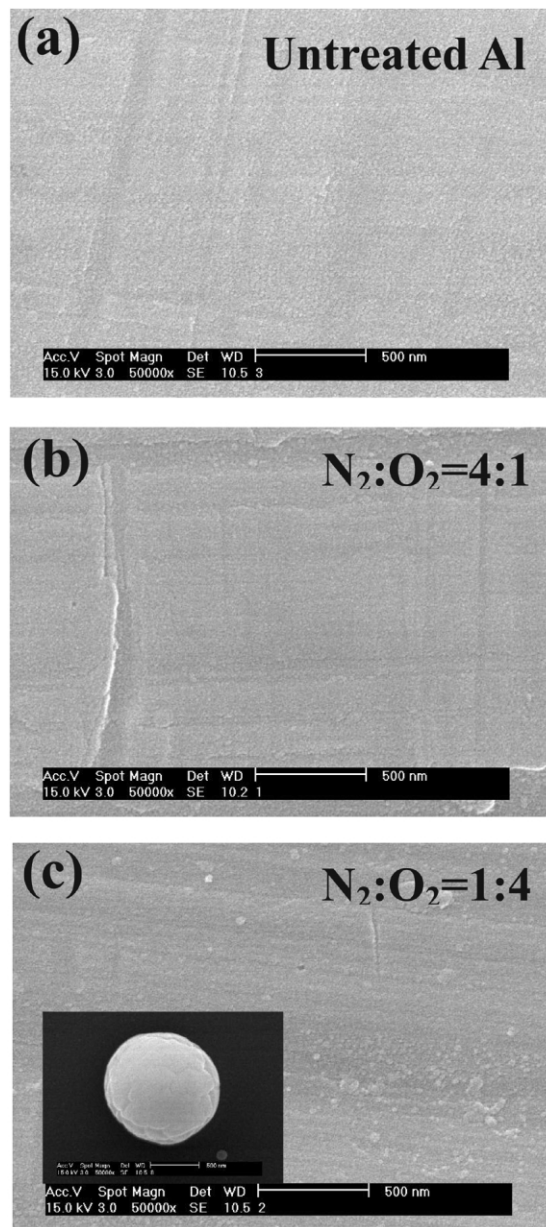


Fig. 4. Surface morphologies by FE-SEM under the conditions of untreated (a), treated at $N_2/O_2=4:1$ (b), and treated at $N_2/O_2=1:4$ (c) on Al substrates. The inset shows aggregated particle image of the same surface.

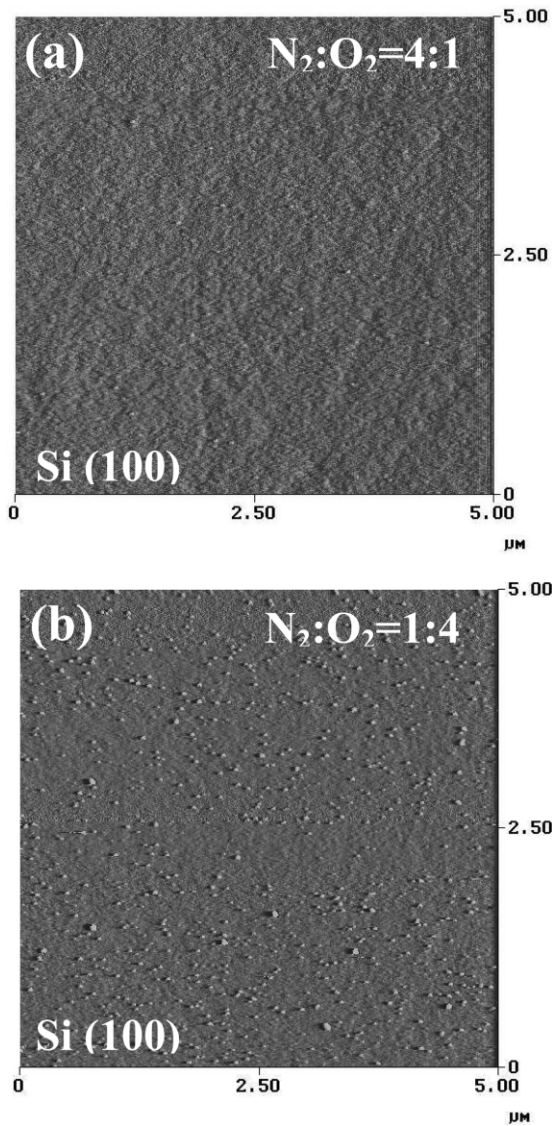


Fig. 5. Surface morphologies analyzed by AFM under the conditions of $N_2/O_2=4:1$ (a) and $N_2/O_2=1:4$ (b) on Si (100) substrates.

The other reason was that the collision frequency was concerned with the proportion to mean speed of molecules and with the inverse proportion to molecule mass; the mean speed of molecules was decreased with increasing the molecule mass. Therefore, it could be expected to increase the plasma density in the case of $N_2/O_2=4:1$ in comparison with $N_2/O_2=1:4$ because of the nitrogen concentration. From the OES results, we could expect that chemical reactions under the condition of $N_2/O_2=4:1$ could be more increased in a gas phase and/or on the surface than the condition of $N_2/O_2=1:4$.

3.5. Contact angle measurements for aging characteristics

Fig. 6 shows the contact angle data of plasma treated surfaces obtained under the optimum conditions with

different gas ratios of $N_2/O_2=4:1$ and $N_2/O_2=1:4$. In these data, there was one important thing that the results of contact angle analysis of the plasma treated substrates on Al, SUS and Cu were very similar with each other. From these results, we could recognize that the surface activation was governed by effects of reactive etching generated by nitrogen molecules under the condition of $N_2/O_2=4:1$, to the contrary, by effects of the particle aggregations composed with hydrogen, oxygen and carbon caused by oxygen atoms, ions, H_2O and CO_2 under the condition of $N_2/O_2=1:4$.

Moreover, we have measured contact angles for 8 days using the plasma treated substrates under the same optimum conditions as mentioned above at room temperature and relative humidity of 64%, continuously. Fig. 7 shows that, within 15 h in our study, the contact angles were particularly increased with increasing the exposed time. In the industrial applications, the aging property is important for the maintenance for a long time with the high surface energy because it has a deep with production cost and storage. Therefore, we could recognize from these data that the highly activated

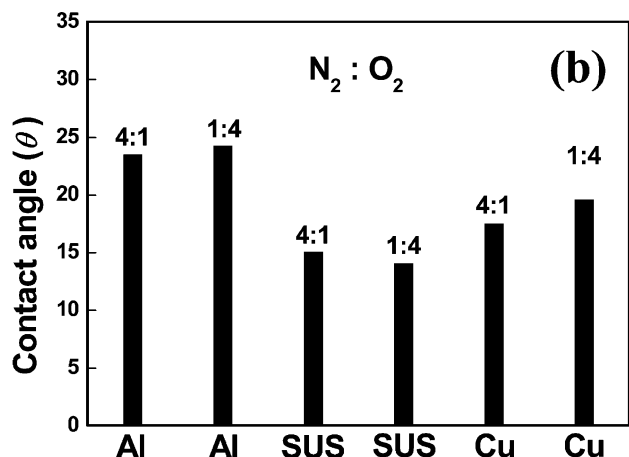
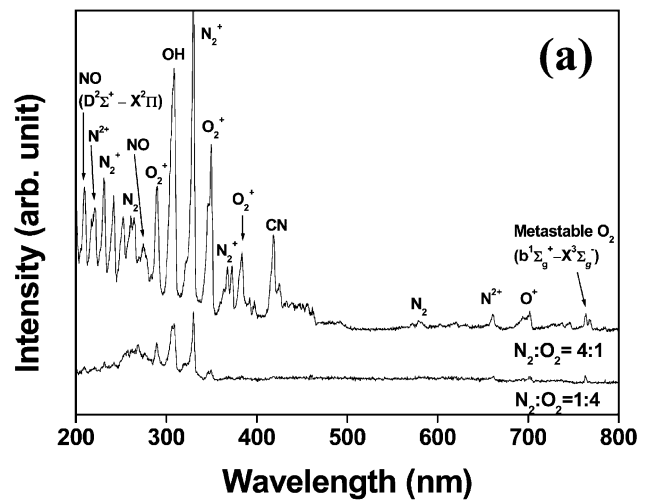


Fig. 6. Optical emission spectra obtained under the conditions of $N_2/O_2=4:1$ and $N_2/O_2=1:4$ (a).

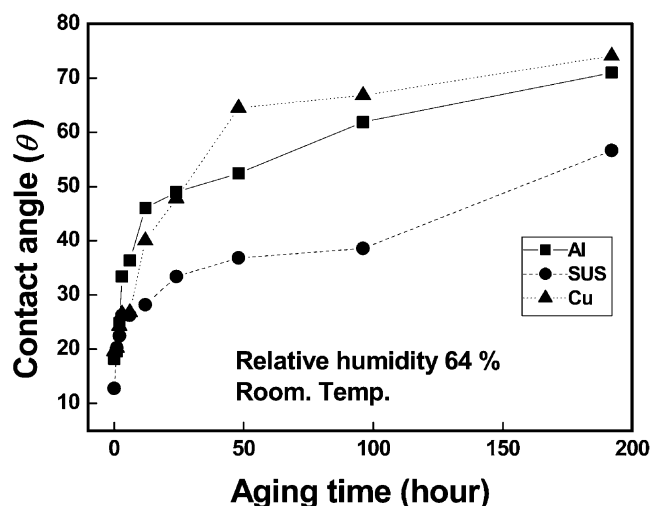


Fig. 7. The variation of contact angles obtained under different gas ratio (a) and exposed time during 8 days of the treated metal surfaces (b) by our atmospheric-pressure plasma jet under the optimum conditions with different gas ratio, relative humidity of 64% and room temperature.

surfaces reacted rapidly even in the stable molecules due to its high surface energies as discussed phenomena in XPS and AFM analysis.

4. Conclusions

In our experiments, we have successfully treated the metal substrates using the mixed gases of nitrogen and oxygen by atmospheric-pressure plasma jet system. In the range of the lowest contact angles for adhesion enhancement were $12\sim 18^\circ$ at the nozzle-to-surface gap of $10\sim 20$ mm with nozzle moving velocity of 5 mm/s. The XPS data revealed that the ablation of organic contaminants and the oxidation were newly occurred with composing C, O and metal oxide. As the results of FE-SEM and AFM analysis, we found that the surface cleaning and particle aggregations were also affected by activated species such as O and N atoms and/or excited molecules, causing bombarding, etching and oxidation, reactively. The results of aging test showed that the

highly activated surfaces were obtained and had short duration time of approximately 15 h at air environment after plasma treating. Based on our experimental data, we could understand the surface phenomena caused by the role of oxygen and nitrogen gases. We also confirm that the metals could be easily treated to clean and even new particles could be aggregated densely on metal surfaces under the air condition by atmospheric plasma jet method.

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