Study on Nitriding of Aluminum by Supersonic Expanding Nitrogen Plasma Jets

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Abstract

Nitriding of aluminum and aluminum alloy using supersonic expanding nitrogen and nitrogen-hydrogen mixture plasma jets were carried out. The following results are obtained. Nitride layer was not formed on the surface of the sample even on the same condition that the nitride layer was formed in the case of titanium. On the other hand, nitride layer was slightly formed on the substrate in the case of hydrogen /nitrogen mixture gas use. However, surface of the substrate came to be rough during operation in this case. Since the same phenomenon occurred in the case of hydrogen /argon mixture working gas, it was thought that the change of the substrate during operation was due to hydrogen infiltration into the substrate. In the case of nitriding of aluminum-magnesium alloy, unlike the case of aluminum substrate use, nitride layer was formed on the substrate even on the condition that pure nitrogen was used as working gas. From these results, this process was found to have a high potential for nitriding to produce aluminum nitride.

1. Introduction

Since thermal plasma jets have high energy density, high chemically reactive particle density and high flux, it is thought to be very useful for improvement of nitriding rate to use the plasma jets for nitriding process. However, since nitriding process is the process with surface chemical reaction, we should take account of the risk that the sample is melted down during operation, and it is very difficult to apply the plasma jets to nitriding process under an atmospheric pressure. While, since the plasma jets are accelerated to supersonic, the plasma jets are released as the low temperature plasma jets with high chemically activated particle density from nozzle outlet owing to adiabatic expansion and frozen flow. So that, it must be useful for enhancement of nitriding rate to use the supersonic expanding plasma jets for nitriding process. In our previous studies [1], [2], in order to investigate the reactivity of the supersonic expanding plasma jets, nitriding of titanium and steels using nitrogen plasma jets at 30Pa chamber pressure was carried out. Consequently, it was proved that the plasma jets had enough reactivity to form a hard and thick nitride layer on the surface of a titanium plate by only a few minutes plasma jet irradiation.

In this study, in order to obtain some useful information for practical applications of this process, nitriding of aluminum and aluminum alloy using nitrogen and hydrogen/ nitrogen mixture plasma jets were carried out at 30Pa chamber pressure.

2. Experimental procedure
Experimental apparatus for nitriding of aluminum and aluminum alloy consisted of vacuum chamber, plasma torch, gas supply system, power supply system and vacuum pump. Sample holder was placed as the axial center of the plasma jets irradiated the center of the sample (this position will be indicated as "the center" in the following sentences) in the vacuum chamber. Pure nitrogen and hydrogen/ nitrogen mixture gas were used as working gases and aluminum plate and aluminum- magnesium alloy plate (Mg: 2.5wt%, Cr: 0.25wt%, Al: Bal.) were used as substrates. The discharge power was 6 kW and nitriding time was 5 min. As working gas, pure nitrogen and hydrogen/ nitrogen mixture gas were used. Flow rate of nitrogen gases were 9.6SLM in both cases and the rate of hydrogen was 3.2SLM in the case of hydrogen/ nitrogen mixture gas use. Surface condition and surface components were investigated by optical microscope and X-ray diffraction, respectively. Surface hardness of the substrate was measured by Vickers hardness tester. Nitriding temperature was measured by pyrometer and controlled by varying the irradiating distance, which was the distance between the head of the plasma torch and the surface of the substrate.

3. Results and discussion

3-1 Nitriding of aluminum

Since aluminum had rigid surface oxide layer, it had been thought that nitriding of aluminum was very difficult. Actually, though some researches on nitriding of aluminum had been successfully conducted so far, these nitriding processes needed melting or vaporization of aluminum substrate during operation in order to remove the surface oxide layer. However, according to our previous study on plasma diagnostics of supersonic expanding plasma jets [3], supersonic nitrogen plasma jets were the low temperature plasma with high radical particle density. Therefore, it was thought that the plasma jets could have enough reactivity to remove the rigid aluminum oxide layer. First of all, in order to confirm the chemical reactivity of supersonic expanding pure nitrogen plasma jets for aluminum, direct nitriding of aluminum without melting or vaporization of aluminum by using supersonic expanding pure nitrogen plasma jets were carried out.

Though surface hardness was raised and the color of the sample turned from silver to gold on this condition in the case of titanium, variation of surface conditions and surface hardening couldn't be observed in this case. So, in order to promote nitriding rate, nitriding of aluminum on the condition of shorter irradiating distance. However, nitride layer wasn't formed and surface hardening didn't occur even in the case that the sample melted down during operation.

From these results, it was proved that the supersonic expanding nitrogen plasma jets used in this study didn't have enough reactivity to reduce the aluminum oxide layer though this plasma jets were very reactive. Then, as another rapid nitriding method to produce aluminum nitride using this plasma jets, nitriding of aluminum using supersonic expanding plasma jets by introducing reducer gas into the nitrogen plasma jets was studied. As reducer gas, though hydrogen and carbon oxide (CO) which was used in carbothermal reduction of aluminum oxide were effective, hydrogen was used because carbon oxide was toxic and had a tendency to cause carburising.

Figure 1 shows the appearance of the sample nitrided by hydrogen/ nitrogen mixture plasma jets on the condition that irradiating distance was 300mm (nitriding temperature at the center was 933K). In the case of using pure nitrogen as working gas, nitride layer wasn't formed on the substrate even on the condition that the substrate was melted down during operation. On the other hand, aluminum nitride layer was formed on the substrate in the case of hydrogen/nitrogen mixture gas. This result suggested that these supersonic expanding
plasma jets had enough chemical reactivity to destruct the aluminum oxide film prevent from nitriding of aluminum. However, surface of the substrate came to be rough during operation in this case. The rough surface was formed due to generation of blisters during operation. The blisters appeared at the center of the substrate 3 minutes after the operation had been started and the area where the blisters were generated expanded gradually toward the edge, and finally, the aluminum substrate was covered with the blisters. The blisters were thought to be generated by volume expansion due to nitriding or blister creation due to hydrogen absorption by aluminum substrate. Then, for the purpose of confirming whether the cause of blister generation was due to hydrogen absorption by aluminum substrate or not, hydrogen/argon mixture plasma jets irradiation to aluminum substrate was conducted. Consequently, almost the same phenomenon as that in the case of hydrogen/argon mixture plasma occurred and the aluminum substrate had covered with blisters after operation. Figure 2 shows the appearance of the hydrogen/argon mixture plasma jets irradiated sample. Thereby, it was thought that hydrogen infiltration into the substrate was dominant in this blister generation process. However, since these blisters were small and crowded in comparison with those in the case of hydrogen/nitrogen plasma jets, blisters generation was affected by chemical reaction between nitrogen and aluminum as well.

3-2 Nitriding of aluminum-magnesium alloy

Next, rapid nitriding to obtain aluminum nitride without blister generation was tried by using aluminum-magnesium alloy plate as substrate. Figures 3, 4 show appearances and X-ray diffraction patterns of the aluminum-magnesium alloy sample nitrided on the same condition as the case of the nitriding of aluminum by pure nitrogen plasma jets. In this case, unlike the case of pure aluminum substrate, nitride layer was formed and surface of the substrate had become frosted on the substrate on the condition that irradiating distance was 250mm, besides this phenomenon was observed even in the case of 350mm in irradiating distance. According to the previous reports on direct nitriding to produce aluminum nitride [4], [5], deoxidation of aluminum oxide surface layer by magnesium contented in aluminum occurred over 670K and aluminum oxide was reduced. Then, chemical reaction between aluminum and nitrogen occurred and aluminum nitride layer was produced. Almost the same reactions might occur in our experiment.

4. Conclusions

In order to obtain some useful information for practical applications of nitriding using supersonic expanding plasma jets, the nitridings of aluminum and aluminum-magnesium alloy by using supersonic plasma jets were studied. Consequently, though nitride layer couldn't be formed on the surface of the aluminum substrate in the case of pure nitrogen plasma jets, nitride layer could be formed in the case of hydrogen/nitrogen plasma jets. However, surface of the substrate came to be rough because the aluminum absorbed hydrogen during operation. While, in the case of aluminum-magnesium alloy use, aluminum nitride layer could be formed on the surface of the sample without rough surface even on the condition that pure nitrogen plasma jets were used. From these results, this process was found to have a high potential for rapid nitriding without melting or vaporization of substrate to produce aluminum nitride.

References


Fig. 1 Appearance of the sample nitrided by hydrogen/ nitrogen mixture plasma jets.

Fig. 2 Appearance of the sample irradiated by Argon/ nitrogen mixture plasma jets.

Fig. 3 Appearance of the sample nitrided by hydrogen/ nitrogen mixture plasma jets.

Fig. 4 X-ray diffraction pattern of the aluminum-magnesium alloy sample nitrided by nitrogen plasma jets.