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Improvement of Wear Resistance of Steels by Nitriding Using Supersonic Expanding Nitrogen Plasma Jets

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Plasma jets have been successfully used as heat sources of thermal plasma spraying process. However, since the plasma jet is accelerated to supersonic under a low pressure environment, the plasma jets can be used as low temperature plasmas with high chemical reactivity due to supersonic adiabatic expansion and frozen flow. From this viewpoint, nitriding of titanium plates using supersonic expanding nitrogen plasma jets under a low pressure environment was carried out in our previous study. As a result, it was proved that the plasma jets had enough reactivity to form a hard and thick titanium nitride layer on the surface of a titanium plate by only a few minutes of plasma jet irradiation at 30 Pa chamber pressure. In this study in order to develop a practical low temperature and high rate nitriding process, nitriding of nitriding steel, carbon steel and stainless steel using this process was carried out and wear resistance of these nitrided samples was investigated. Consequently, surface hardening was obviously promoted on the condition that hydrogen/nitrogen mixture gas were used as working gas in the cases of all substrates. Especially, hard layers with over 1 000 Hv in hardness were formed without any surface damages on the surfaces of the samples by only 5 min of operation in the cases of nitriding steel and stainless steel. Besides, according to the results of wear testing, wear resistance of these steels was dramatically improved.

KEY WORDS: surface modification; plasma nitriding; nitriding steel; carbon steel; stainless steel; tool steel; wear.

1. Introduction

Steels are widely used in various industries because of its mechanical strength, toughness and low price. Recently, since surface modification of steel is increasingly demanded in lots of applications, surface hardening process becomes more important. As for surface hardening techniques, nitriding has been successfully used as a high rate and low temperature surface modification process which replaces quenching and carburizing since this method was developed in the former part of the 1920's. Especially, since nitriding could be conducted at a significantly lower temperature with a much shorter operating time in comparison with the conventional gas nitriding method by development of ion nitriding in the latter part of the 1960's, application field of nitriding was widely expanded.[1,2] Besides, quite recently, by the development of duplex surface tailoring which PVD film was deposited on the surface hardened substrate, the application field is still widely expanded even now. However, though ion nitriding is a high rate surface modification technique, it takes a few hours to accomplish the treatment. Hence, surface coated steels by plating are widely used in comparison with nitrided steels in the industries where resistance to wear, corrosion are required.

On the other hand, though plasma jets have been used as heat sources of thermal plasma spraying process, the temperatures of the plasma jets fell down drastically due to adiabatic supersonic expansion but plasma jets can transport many radical particles on the substrate due to frozen flow under a low pressure environment. That is, this supersonic expanding plasma jet can be used as low temperature plasma with high radical particle density. In our previous study, in order to develop high rate and low temperature nitriding process, nitriding of titanium using supersonic expanding nitrogen plasma jets at 30 Pa in chamber pressure was carried out. Consequently, it was proved that the plasma jets had enough reactivity to form a hard and thick titanium nitride layer on the surface of a titanium plate by only a few minutes of plasma jet irradiation.

In this study, in order to obtain useful information for the practical applications of the process using supersonic expanding plasma jets, nitriding of nitriding steel (SACM645), carbon steel (S45C), mould steel (SKD61) and austenitic stainless steel (SUS304) using supersonic expanding nitrogen plasma jets were carried out. Besides, tribological property of the nitrided SACM645 sample was also investigated.

2. Experimental Procedure

Experimental apparatus for the surface nitriding consists of a vacuum chamber, a plasma torch, a gas supply system,

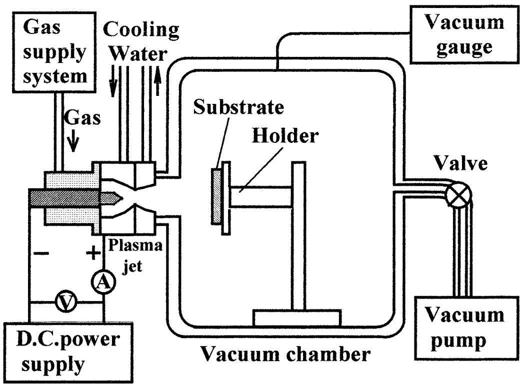


Fig. 1. Schematic diagram of the apparatus for surface nitriding.

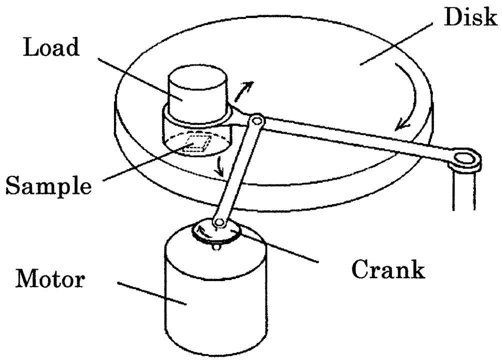
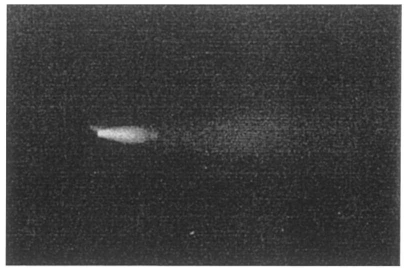


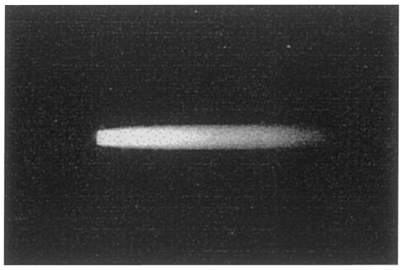
Fig. 2. Schematic diagram of the wear testing apparatus.

a power supply system and a vacuum pump shown as **Fig. 1**. A sample holder was placed in the vacuum chamber and the plasma torch has the optimally designed supersonic expansion nozzle for use at 30 Pa chamber pressure. Three samples were horizontally set on the sample holder and the sample on the left-hand side was aligned to the central axis of the plasma jet irradiaing this sample (This sample will be indicated as "center" in the following sentences.). The discharge power was 6 kW (40 V, 150 A), and the mass flow rate of nitrogen was 9.6 SLM in the case of the nitriding using nitrogen plasma jets. In the case of the nitriding using hydrogen/nitrogen mixture plasma jets, the discharge power was 7.5 kW (50 V, 150 A), and the mass flow ratio of hydrogen/nitrogen was 1/3 (3.2 SLM/9.6 SLM). The nitriding time was 5 min. Irradiating distance, which is the distance between the nozzle outlet and the surface of the sample, was varied from 180 to 350 mm. Nitriding temperatures during operation were measured by a CA thermocouple fixed on the other surface of the samples. The surface structures of nitrided samples were investigated by means of X-ray diffraction (CuKα, 40 kV, 30 mA). The surface hardness of the nitrided sample was measured by Vickers hardness testing. Wear resistance testing was conducted by the so-called Block on Disk method using the apparatus shown schematically in **Fig. 2** The disk covered with #2 000 sandpaper was 200 mm in diameter, the rotational speed was 1 450 rpm and the load was 500 g. The wear mass loss was measured every 3 000 m wear distance by the time when total wear distance reached 15 000 m.

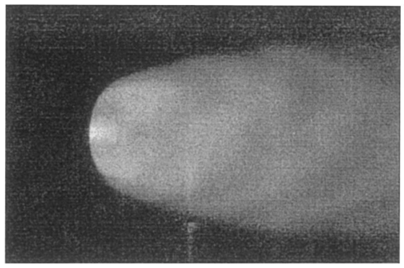
Samples are ϕ25 mm$\times$3 mm^t coin shaped SACM645, S45C, SKD61 and SUS304. The surfaces of these samples were polished by #1 000 emery paper before operation.



a) P=3kPa



b) P=800Pa



c) P=30Pa

Fig. 3. Appearance of the plasma jets in each chamber pressure.

3. Results and Discussion

3.1. Plasma Jets in Each Chamber Pressure

Figure 3 shows appearance of the plasma jets in each chamber pressure. Though the plasma jet was 50 mm length and 10 mm width in the case of 3 kPa in chamber pressure, it was expanded and elongated as chamber pressure decreased, and finally became over 1 000 mm length and 300 mm width in the case of 30 Pa. Besides, since the velocity of the plasma jets increased to supersonic with decreasing chamber pressure, shock wave, so called "shock diamond", generated in the plasma jets on the condition that nozzle outlet pressure was different from chamber pressure and the shock wave deteriorate the length of the plasma jets. Therefore, in this study, the plasma torch equipped the Laval nozzle which was designed to eliminate the difference between nozzle outlet pressure and chamber pressure in each condition. **Figure 4** shows the appearances of the plasma jets from the plasma torch without Laval nozzle and that with Laval nozzle.

3.2. Relation Between Irradiation Distance and Nitriding Temperature

In our previous study,[3,4] plasma diagnostic study in a plasma torch in 30 Pa in chamber pressure was carried out by using optical emission spectroscopy. Resultly, though heavy particles temperatures at the nozzle inlet were ap-

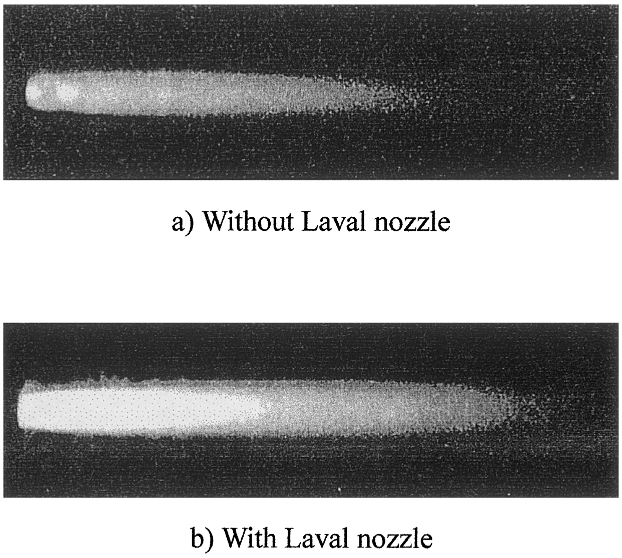


Fig. 4. The appearances of the plasma jets from the plasma torch without Laval nozzle and that with Laval nozzle.

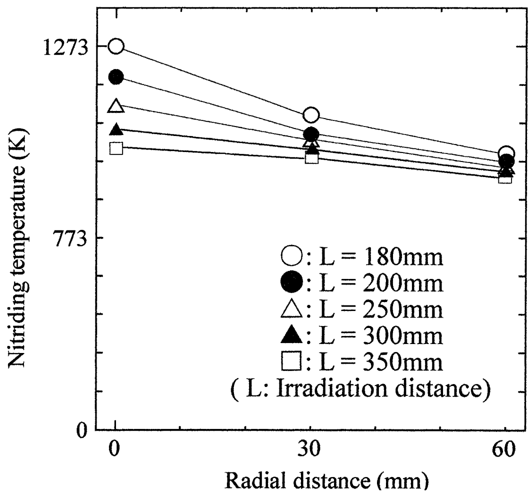


Fig. 5. Relation between radial distance and irradiation distance in the case of N_2/H_2 mixture plasma jets use.

proximately 10^4 K, the temperatures drastically fell down in the nozzle, and finally, vibration temperature and rotation temperature of the plasma jets became 4 000 K and 2 000 K respectively at the nozzle outlet. Therefore, this plasma is thought to be treated as low temperature plasma according to circumstances. However, since plasma jets still have enough heat energy to melt the substrate if irradiation distance is very short and axial variation of plasma jets' temperatures are drastic, it is important to know relation between irradiation distance and nitriding temperature so as to operate the low temperature nitriding process using supersonic expanding plasma jets. Then, the relation between irradiation distance and the nitriding temperature was confirmed. **Figure 5** shows relation between radial distance and irradiation distance in the case of N_2/H_2 mixture plasma jets use. Nitriding temperatures at the center and the edge (60 mm distant from the center) were about 1 273 K and 993 K respectively in the case of 180 mm in irradiation distance. However, the temperatures fell down to about 993 K and 923 K respectively in the case of 350 mm though samples

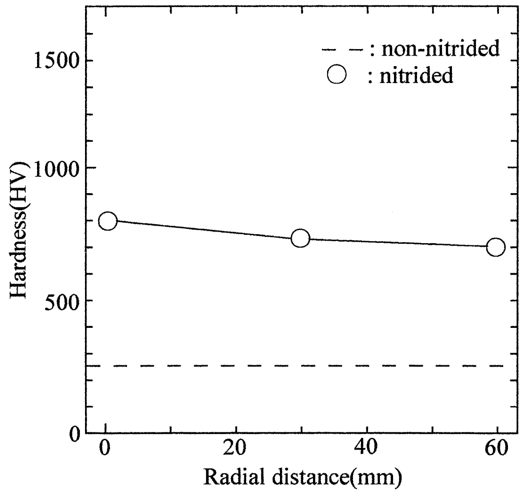


Fig. 6. Radial profiles of surface hardness of the nitrided SACM645 samples in the case of H_2/N_2 mixture plasma jets.

were still irradiated by plasma jets sufficiently even on this condition.

3.3. Nitriding of SACM645 and Wear Resistance of the Nitrided Sample

Supersonic expanding pure nitrogen plasma jets had enough reactivity to form thick nitride layer on the surface of the titanium plate by only a few minutes nitriding treatment.[5] Hence, in order to obtain more practical information, nitriding of SACM645 steel using pure nitrogen plasma jets were conducted. Besides, nitriding using hydrogen/nitrogen mixture plasma jets were carried out. In conventional nitriding processes, nitriding rate was enhanced by hydrogen addition to nitrogen or nitrogen plasma. Generally, the effect of hydrogen addition on the nitriding rate was thought that chemically reactive species, *i.e.* molecular radicals, generated by hydrogen addition to nitrogen promote nitriding. In the previous study, one of the authors of this paper studied the N_2+3H_2 arc structure and the flow field in a plasma torch by means of optical emission spectroscopy.[3,4] Consequently, since many kinds of molecular radical, such as not only N_2 but also NH, were observed near the outlet of the plasma torch, hydrogen/nitrogen mixture plasma is expected to be much more reactive than pure nitrogen plasma also in nitriding using thermal plasma jets.

Figure 6 shows radial profiles of surface hardness of the non-nitrided and nitrided samples on the condition that irradiation distance was 180 mm in the case of pure nitrogen plasma jets and hydrogen/nitrogen mixture plasma jets. In the case of pure nitrogen plasma jets, SACM645 surface was hardly hardened on the condition that nitride layer was formed on the titanium substrate. Even on the condition that sample was so close to plasma torch that the sample melted down during operation, surface hardening did not occur. While, in the case of hydrogen/nitrogen mixture plasma jets use, unlike the case of the nitriding using pure nitrogen plasma jets, the hard layer which was over 800 HV in Vickers hardness was formed on the surface of the sample by only a few minutes operation at each position. According to optical micrographs of the surfaces of the nitrided samples (**Fig. 7**), surface morphology of the sample

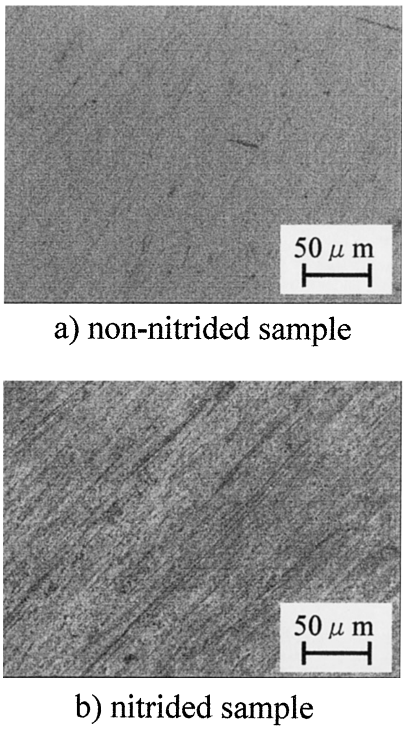


Fig. 7. Optical micrographs showing the surfaces of the non-nitrided and nitrided SACM645 samples.

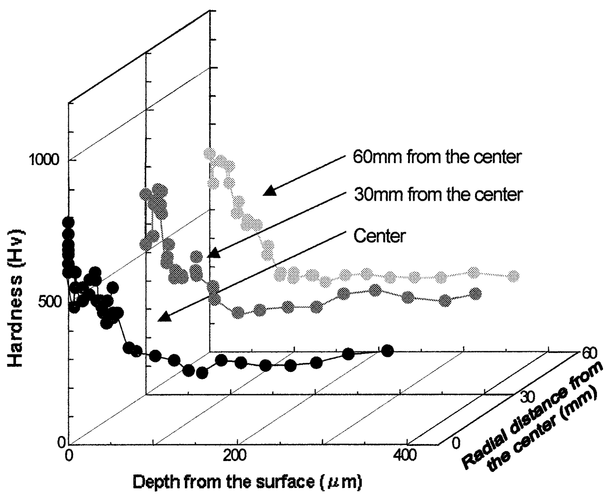


Fig. 8. Vickers hardness profiles of the nitrided samples in the case of H_2/N_2 mixture gas with 3/1 mass flow ratio.

was unchanged except the slight change of the surface color during operation though surface hardening occurred at each position. Besides, the surface hardening occurred even on the condition of 350 mm in irradiation distance. These phenomena were frequently investigated in the case that NH radicals generated in plasma jets contributed to the nitriding in the conventional nitriding processes. These results suggest that NH radicals contribute to surface hardening also in the case of nitriding using supersonic expanding plasma jets. **Figures 8**, and **9** show depth profiles of the hardness of the sample and optical micrograph of the cross section of the "center" sample nitrided by hydrogen/ nitrogen mixture plasma jets. From this figure, surface hardening was thought to occur due to some kind of chemical reaction or phase transfer. However, though disappearance of Fe (200)

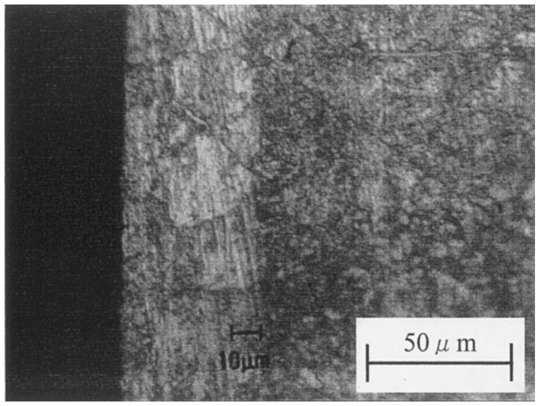


Fig. 9. Optical micrographs showing the cross-section of the nitrided SACM645 samples.

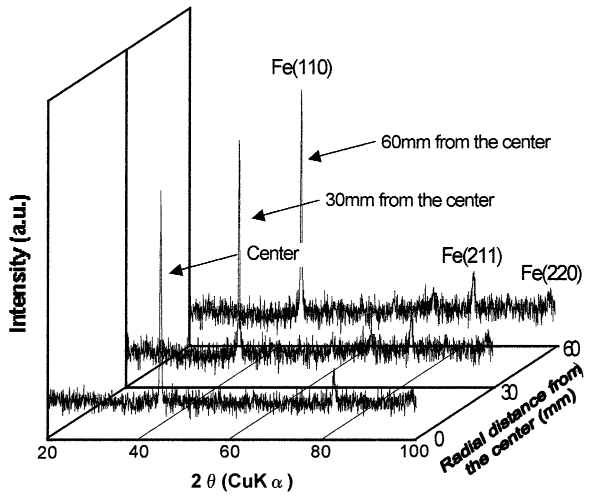


Fig. 10. X-ray diffraction patterns of the nitrided SACM645 samples.

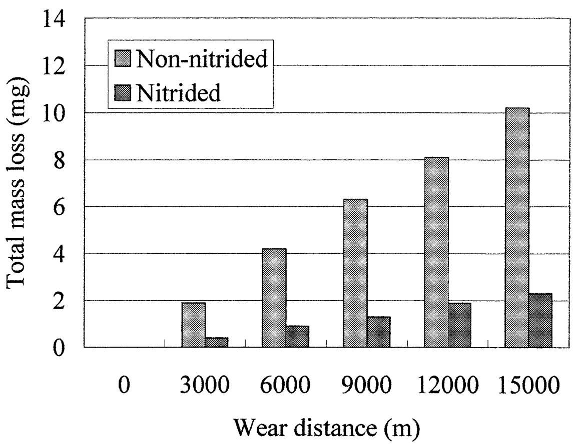


Fig. 11. Wear test results of the non-nitrided sample and the SACM645 sample nitrided by H_2/N_2 mixture plasma jets.

peak during nitriding was confirmed, nitride and hydride peaks couldn't be confirmed even in the XRD patterns of the nitrided sample (**Fig. 10**).

Figure 11 shows wear mass loss of a non-nitrided sample and the samples nitrided at the position 60 mm distant from the center on the condition that hydrogen/nitrogen mixture plasma jets were used. While the total wear mass loss of the non-nitrided sample and nitrided sample at 15 000 m wear distamce was 10.2 mg, the mass loss of the nitrided sample by hydrogen/nitrogen plasma jets was of mass 2.3 mg. From these results, the improvement of wear resistance ability by nitriding could be confirmed. Though difference between nitrided samples and non-nitrided sample couldn't be confirmed from the results of X-ray diffraction patterns even in this case, it is considered that surface hardening occurred due to NH radical reaction because surface hardening didn't occur except the case that nitrogen and hydrogen were used simultaneously.

3.4. Nitriding of S45C, SKD61 and SUS304 and Wear Resistance of the Nitrided Samples

Since SACM645 is a steel so designed that surface hardening due to nitriding occurs easily, SACM645 is very expensive compared to the other steels and mechanical strength of this steel isn't so high. Hence, it is very difficult to use this steel as engineering material. Then, in order to obtain more useful information for application of this nitriding process to practical use, nitriding of S45C, SKD61 and SUS304, which are practical steel materials, were conducted. However, since surface hardening of the samples didn't occur and wear resistance improvement of them weren't observed in all cases of pure nitrogen plasma jets use, only the results in the cases of hydrogen/ nitrogen mixture plasma jets use are introduced in the following sentences.

Figure 12 shows radial profiles of surface hardness of these samples nitrided by hydrogen /nitrogen plasma jets. Though the surface hardening was promoted by addition of hydrogen also in the case of S45C, maximum surface hardness of the nitrided S45C sample was about 500 HV which was very low compared to that of nitrided SACM645 samples. As for the results of the SKD 61, surface hardening was occurred only on the condition that hydrogen/ nitrogen mixture plasma jets were used and the surface was slightly harder than that of S45C. However, from the results of XRD, iron nitride couldn't be observed. While, in the case of SUS304, unlike the case of S45C and SKD61, drastic surface hardening promotion occurred and surface hardness of the sample located at the position which was 60 mm distant from the center came to be over 1 000 HV after nitriding. From the results of XRD, unlike the other cases, iron nitride was confirmed on the surface of each nitrided sample. By the way, the reason why surface hardening hardly occurred at the center in any cases was thought to be because the atmosphere at the axial center of the plasma jets became hydrogen poor as the plasma jets go downstream since hydrogen and hydride molecular had a tendency to diffuse radially from the axial center.

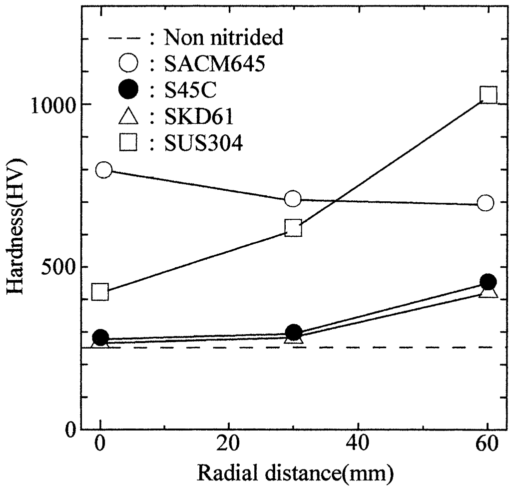


Fig. 12. Radial profiles of surface hardness of the nitrided samples in the case of H_2/N_2 mixture plasma jets.

4. Conclusion

Nitriding of SACM645, S45C, SKD61 and SUS304 steel using supersonic expanding nitrogen plasma jets were carried out. Consequently, we could conclude as follows.

(1) By using nitrogen-hydrogen mixture plasma jets, surface hardening occurred extremely without changing surface mophology of the substrate. According to the experimental results by conventional nitriding processes, it was considered that the phenomena occurred because NH radicals generated in plasma jets contributed to the nitriding.

(2) Nitriding using supersonic expanding plasma jets improve not only surface hardness but also wear resistance of steels.

(3) From these results, this process was found to have a high potential for surface modification even in the case of not only SACM645 but also commercial S45C, SKD61 and SUS304 steels.

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