The Study about Surface Modification of Steel by Water Plasma

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Abstract

Recently, a lot of research has been carried out to improve the properties of steel surface such as ion-nitriding, gas nitriding. However, they need high vacuum rate or very expensive equipment and longer treatment time. In this study, new nitriding process proposed which have extremely shorter treatment time and very simple equipment by using water plasma. For the water plasma, JIS-SCM420 specimen was used as cathode, and rolled punching stainless steel plate (SUS304) was used as anode. Voltage was applied between electrodes by DC pulsed power supply. Pulsed power supply was used to prevent discharge from concentrating on one point. Urea $(H_2N)_2C=O$ used as supply source of nitrogen and potassium hydrate (KOH) for adjusting electric conductivity. And it was put into distilled water as electrolyte. Treatment voltage was 600 V, and experiments were conducted by varying conditions such as treatment time and concentration of electrolyte. After water plasma treatment, a lot of fine discharge pores can be seen on the treated steel surface. And also, a few μm modified layer is formed on the steel surface after water plasma treatment within 5min. At the results of XRD analysis, iron nitrides are detected with Fe peaks and the hardness of nitride layer shows about 800HV.

Key words: Water plasma, Nitride layer, Urea, Potassium hydrate

1. Introduction

Steels are widely used because of good strength, toughness and workability. But steels which are used as slide parts are required additional wear resistance or fatigue resistance. To improve these mechanical properties, surface-hardening process such as carburizing, nitriding treatment has being used. For example, ion nitriding is a representative process in the most of nitriding process on nowadays. Treatment time of ion nitriding is much shorter than that of gas nitriding. In addition, harmful gases such as ammonia are not used in the treatment; therefore it is not harmful to environment as well known. [1]. However, this process needs vacuum furnace and spends more time on the pre- and post- processes for vacuuming and cooling of furnace.

Plasma which has many kind of advantage on surface modification field can be generated in a liquid by high frequency or microwave irradiation from an underwater electrode. Recently, it has been reported that in-liquid (or water) plasma can synthesize substances at a higher rate than conventional gas phase plasma [2]. In particular, it has been known that when a substrate is submerged in an organic solvent or an alcohol and plasma is generated under the substrate, diamond [3], diamond-like carbon, carbon nanotubes and SiC can be deposited on the surface of the substrate [4]. Moreover, in-liquid plasma is useful for decomposition of harmful liquids and liquids containing dissolved harmful substances [5ï7]. And it is expected that the treatment time is also can be possible to decrease because of not needed vacuum and cooling during process. To this end the pulsed discharge of high-voltage electricity in liquids needs to be considered [8, 9].

In this study, new nitriding process that can be conducted in very short treatment time with simple equipment by using water plasma is proposed.

2. Experimental procedures

2.1 Specimen preparation

SCM420 commercial grade of bar type was used as cathode with the size of ϕ5x30mm, and SUS304 stainless steel plate (300x150x10.6mm) was used as anode after rolling and punching. Voltage was applied between SCM420 cathode and SUS304 anode electrodes by DC pulse power supply (Max 600V and 20A).

2.2 Water plasma

Pulse power supply was used to prevent discharge from concentrating on one point (pulse width: 2μs, pulse frequency: 15 kHz). Exposure area of specimen was adjusted by putting insulating tape before treatment. After preparing the specimen, the Urea ($(H_2N)_2C=O$) used as supply source of nitrogen and potassium hydrate (KOH) for adjusting electric conductivity were put into distilled water as electrolyte. Then, water plasma was performed at variety conditions such as treatment time and concentration of electrolyte under the voltage of 600V. The amount of Urea and potassium hydrate were 200g and 10~40g respectively in distilled water per 1ℓ. Fig.1 shows overview of experiment system.

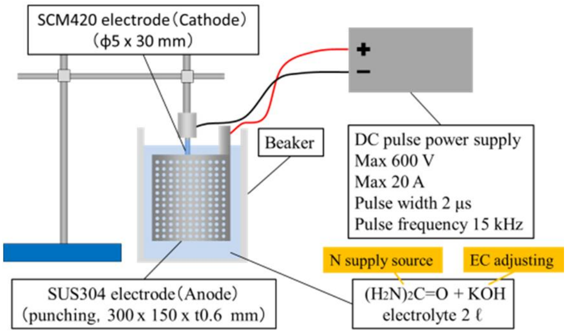

Fig.1 Overview of experiment system.

2.3 Microstructure observation and hardness test

The optical microscopy (OM) and scanning electron microcopy (SEM) (Hitachi, SU6600) were used to observe the micro-structure and morphology after water plasma. Layers were identified by an X-ray diffractometer (Rigaku, UltraX 18 TTR) using monochromatic Cu-K$_{Ŭ}$ radiation. The X-ray diffraction (XRD) measurements were performed using a goniometer at a scanning range of 40°Ò2dÒ80° at 40KV and 200mA with the step-size of 0.02°.

The micro hardness of the surface layer was measured using by a Vickers micro hardness tester (Akashi, HM-125).

3. Results and discussions

3.1. Changes of current during water plasma

To investigate the relationship between current density and treatment time during water plasma, the current was measured according to the treatment time. Fig.2 shows the average current as discharge time under the condition of Urea 200g/ℓ and KOH 20g/ℓ. The average current indicates around 0.6A at first and gradually decreased to about 0.25A until 360sec, after then it shows steady current state. In this result, water plasma discharge is divided into 3 regions as follows. Firstly, weak discharge generates at the edge of surface only (discharge start region). Secondly, the discharge becomes stronger and generates at all of areas (discharge intensification region). And finally, discharge becomes a little weak and stable discharge continues (discharge stability region).

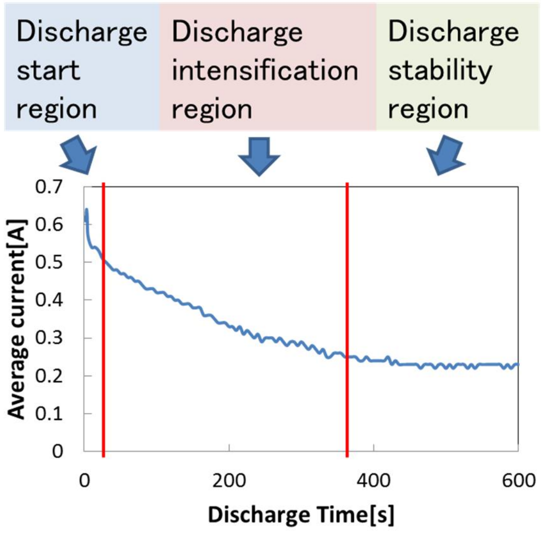

Fig.2 Changes of average currents during water plasma.

3.2. Effects of water plasma on the surface

Fig. 3 shows the changes of surface morphology after water plasma at various treatment times to investigate discharge state on the surface (Urea 200 g/ℓ, KOH 10 g/ℓ). After water plasma, discharge pores are generated on the surface area. However, most of discharge pores can be seen only at edge area of surface until 30sec. After then the time of 30sec, discharge generates all of the areas. And at the 120 sec, uniform discharge pores can be seen both area of center and edge. This tendency about the formation of discharge pores shows similar tendency compared with average current as discharge time as shown in Fig. 2.

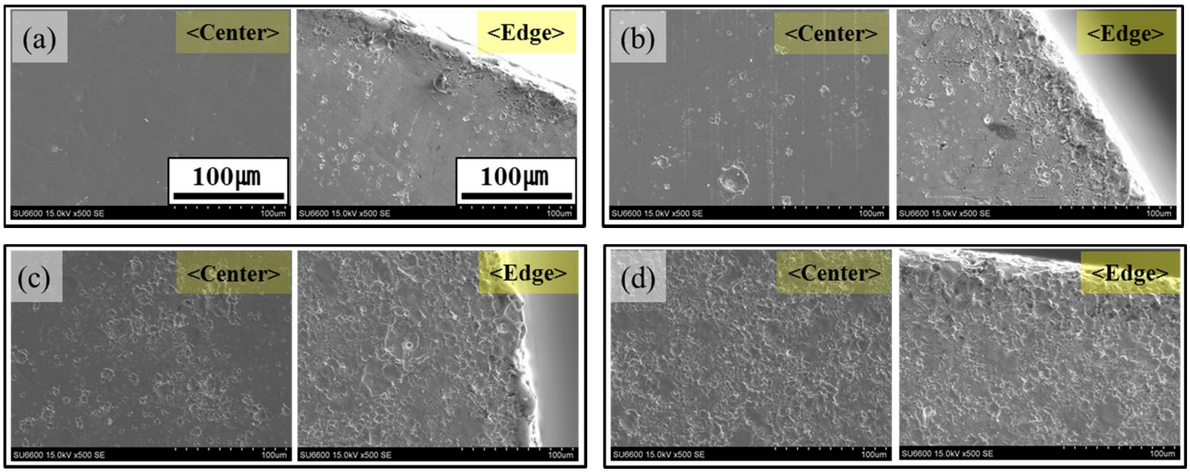

Fig.3 SEM micrographs about the changes of surface condition with respect to treatment time of (a) 10sec, (b) 30sec, (c) 60sec and (d) 120sec.

Fig. 4 shows the effects of potassium hydrate (KOH) concentration with urea 200 g/ℓ. The solution of KOH has the effect of electric conductivity. As shown in Fig. 4, discharge pores being coarsen with increasing the amount of KOH from 10g/ă to 40g/ă. It means that the high concentration of KOH have a strong discharge effect. And the edge effect also not investigated at the high concentration of KOH compared with the SEM micrographs as shown in Fig. 3. Consequently, high KOH concentrations have coarsen discharge pores by strong discharge with lack of uniformity. On the other hands, in low concentration of KOH can be possible fine discharge pores with uniform discharge except the edge effect at the short treatment time.

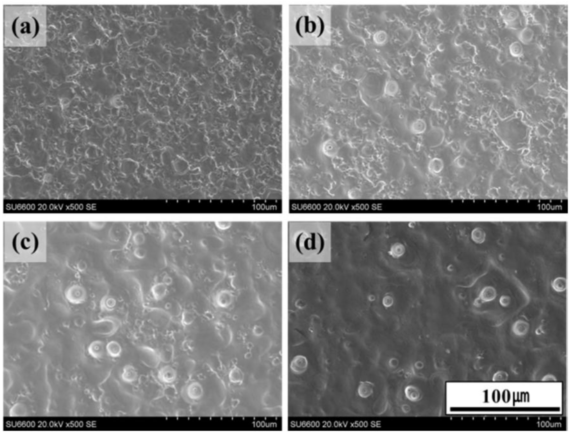

Fig. 4 SEM micrographs after water plasma at urea 200 g/ă and different KOH concentration of (a) 10g/ă, (b) 20g/ă, (c) 30g/ă and (d) 40g/ă for 30min.

3.3. Growth of modification layer

Fig.5 shows the SEM and optical micrographs on the surface area and cross-section with modified-layer respectively, after water plasma at various treatment time under the condition of urea 200 g/ℓ and KOH 20 g/ℓ.

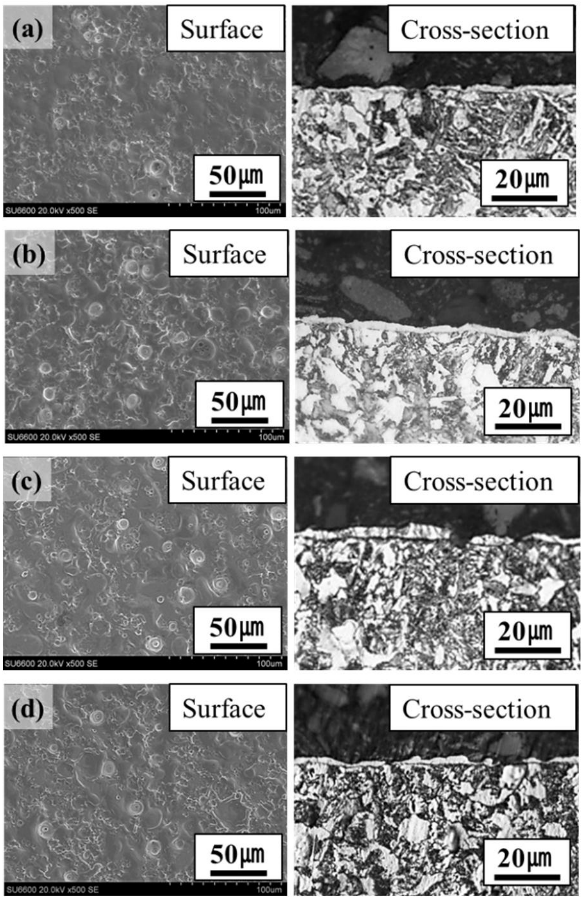

Fig.5 SEM and Optical micrographs on the surface and cross-section after water plasma under the condition of urea 200 g/ℓ and KOH 20 g/ℓ at various time of (a) 2min, (b) 5min, (c)20min and (d) 30min.

As shown in Fig. 5, a lot of fine discharge pores can be seen on the treated-surface. And modified-layers of a few μm are also investigated at the outmost surface of cross-section. The formation of modified-layer is extremely short time compared to general surface modification process with nitriding process. The thickness of modified-layer shows 2~3μm after water plasma and it is not changed remarkably as increasing the treatment time from 2min to 30min. It is indicate that the thickness of the modified layer is not affected significantly by treatment time during water plasma.

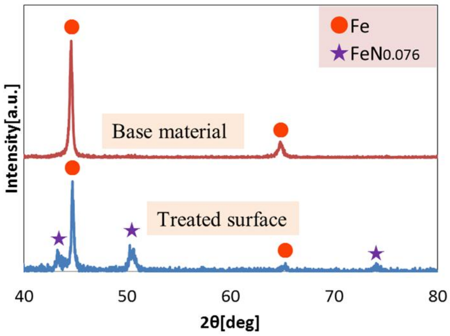

Fig.6 XRD analysis of modified-layer and SCM420 base metal after water plasma in urea 200 g/ă and KOH 20 g/ă for 5min.

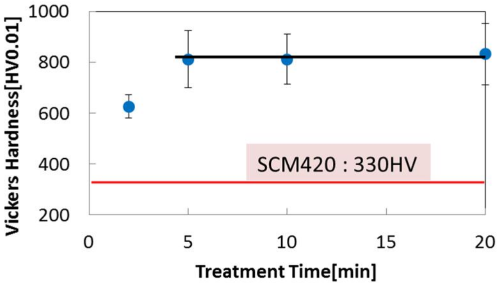

Fig.7 Hardness value of modified-layer after water plasma for various treatment time.

Fig.6 shows the results of XRD analysis of the modified-layer and SCM420 base metal after water plasma for 5min under the condition of urea 200 g/ℓ and KOH 20 g/ℓ. From the result of XRD, $FeN_{0.076}$ peaks are detected with α-Fe peaks. It means that the modified-layer is composed with iron nitrides ($FeN_{0.076}$). The hardness of nitride layer shows about 800HV at the treatment time of 5min as shown in Fig. 7. And the hardness values are also not changed as increase the treatment time. This tendency of hardness value shows similar tendency with the thickness of modified iron nitride layer. It means that the micro-arc discharge generates only at most surface without the diffusion of nitrogen ion. It is expected that the specimen is cooled by surrounding solution at the same time while the water plasma is performing. Therefore, the nitrogen cannot permeate and diffuse from surface to interior of the specimen.

4. Conclusions

After the water plasma, modified thin layer was formed in very short time by using simple equipment. It is expected that the process can be applied to thin plate or minimal parts. The obtained results are as follows;

1. Discharge of water plasma process is divided into 3 regions as follows; first: discharge start region, second: discharge intensification region and finally: discharge stability region.
2. Discharge pores were coarsening with increasing the amount of KOH during water plasma.
3. After water plasma, iron nitride ($FeN_{0.076}$) layer of a few μm(2~3μm) was formed at the outmost surface and the hardness value shows about 800HV.

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