High density plasma beam source for nitriding

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A high density plasma beam source has been developed for the purpose of surface treatment and study of low energy ions and neutrals with surfaces. The plasma is generated by pulse microwave power at 2.45 GHz. A pair of Helmholtz coils is used for generating axial magnetic field of 436 G which is also responsible for the production of plasma inside a stainless steel tube of 26 mm internal diameter. The plasma particles follow the axial magnetic field lines and hence, form a beam of same diameter as the internal diameter of the SS tube. The current measured by an interceptor plate (negatively biased) is about 60 mA while the plasma density is determined to be approximately $1.1 \times 10^{12} \text{ cm}^{-3}$ at the center and falling off to about $1 \times 10^{11} \text{ cm}^{-3}$ at 1 cm away from the center. The plasma source using a mixture of nitrogen and hydrogen (1:2) was used successfully to nitride a sample (diameter 16 mm) of SS201 at a low temperature of 400°C. The surface hardness achieved is rather high (1990 HV) which is more than five-fold increase compared to untreated surface (358 HV). The depth of the nitriding layer was found to be 26 microns. XRD results indicate efficient conversion of chromium to chromium nitride by the high plasma density of the present source accounting for the very efficient nitriding process.

Keywords: Microwave plasma, Nitriding, X-ray diffraction, Microhardness, Iron nitride, Chromium nitride

1 Introduction

Nitriding is a thermo-chemical process by which nitrogen atoms are diffused inside a steel surface (process temperature ~ 500-600°C) for the purpose of increasing its surface hardness. The process is used extensively in the industry for improving service lives of wear and tear prone components and also for improving anti-corrosion properties in some applications. Traditionally, gas and liquid based treatments have been used which, however, are not very energy efficient and also rather environmentally polluting. A more modern technique based on plasma treatment has been found increasing usage because of its ability of having a better control on the process, its energy efficiency and its environment-friendliness.

The most widespread plasma technique is glow discharge plasma nitriding (GDPN). Basically, it is a dc glow discharge system carried out in a vacuum steel chamber at a few mbar of pressure of hydrogen and nitrogen mixture. The work-pieces are kept at negative high voltage (~500 V to ~1 KV) which serve as cathode and the wall chambers (anode) are at ground potential. The current density used is in the range 1-3 mA/cm² (typically 2 mA/cm²) while the plasma density close to the surface of the cathode is ~1×10¹⁰ cm⁻³. The nitriding process temperature is obtained via heating as a consequence of ionic bombardment to the work-pieces. It has been established that hydrogen acts as a catalyst and the various mixture ratios are used for treating different types of steels and imparting various metallurgical properties. It has also been established that GDPN is two to three times faster in providing the same case depth as compared to a traditional process such as gas nitriding which is attributed to the presence of reactive species such as ions N⁺, N₂⁺, N₂H⁺, etc. and radicals N, NH, etc.

In order to understand the role of ionic and radical species further other types of plasma sources which are generally called high density plasma sources, have also been studied. These sources are based on RF (13.56 MHz)⁶, PSII (very high voltage)⁷,⁸ and ECR (2.45 GHz, 875 G)⁹ which can provide plasma density as high as $2\times10^{11} \text{ cm}^{-3}$. These high density plasma sources can accelerate the nitriding process even further and it is possible to nitride even at a low temperature in the range 350-450°C. Studies carried out on hard to nitride steels such as austenitic stainless steels by ECR and PSII suggest formation of expanded austenite, i.e. ‘S’ phase at low temperatures which is very hard.

In order to take this aspect of high density plasma source a level higher the present plasma source was conceptualized, designed and built. The minimum plasma density obtained in this source is $1\times10^{12} \text{ cm}^{-3}$ at a threshold magnetic field of about 400 G. After
that the plasma density varies as square of the magnetic field. This kind of source was first studied at Princeton Plasma Physics Laboratory\textsuperscript{10,11} with the objective of generating high flux of low energy neutrals to study their reactions with surfaces which are of interest in many research fields. Although the source was never used to study the nitriding process, it becomes imperative that it is the ideal source not only for neutral-surface reactions but also ion-surface reactions such as nitriding. Many surface reactions of fundamental importance can be studied with such a plasma/neutral beam source.

The present investigation was undertaken with a view to find out if the nitriding process can be enhanced specially at low temperatures by using a much higher density plasma source not used previously.

2 Experimental Details

2.1 Experimental set-up

The microwave plasma beam source is a high density plasma beam source first developed at Princeton Plasma Physics Laboratory in the 1970s with the objective of creating high flux of low energy neutral beams for various applications. A similar kind of source has been developed for studying the surface reactions of ions and neutrals of interest in plasma processing. Fig. 1 shows a cross-sectional view of our set-up.

Pulsed microwaves (2.45 GHz) are fed to a coaxial antenna (floating) via a WR-284 waveguide from a 1 KW magnetron. The antenna sits inside a stainless steel tube of 26 mm internal diameter and length of 100 mm. To create a plasma inside the SS tube an axial magnetic field is applied with the help of a pair of Helmholtz coils. The threshold value for plasma generation is about 400 G. The plasma particles follow the field lines, i.e. along axial direction until it is intercepted by a plate biased negatively with respect to the plasma potential. A few times $10^{-3}$ mbar gas pressure is required to generate the plasma which can be optimized for maximum plasma density by controlling the mass flow rates of gases using mass flow controllers M1 and M2. The whole vacuum chamber is pumped by a diffusion pump in conjunction with a rotary vane pump. A UV-visible optical spectrometer from StellarNet is used to monitor the active species present in the plasma.

This kind of plasma source has been termed as lower hybrid plasma source\textsuperscript{11}. The minimum plasma density is $1 \times 10^{12}$ cm$^{-3}$, i.e. at the threshold value of magnetic field of 400 G. Beyond the threshold value, the plasma density has been shown to vary as square of the magnetic field. The profile of the plasma density is nearly gaussian with peak being at the center, i.e. along the axis. This is an ideal high density plasma source for studying the surface reactions of ions and neutrals at low energies for various applications specially of interest to plasma processing.

Figure 2 shows ion current to the biased interceptor plate for a mixture of nitrogen and hydrogen (ratio=1:2) with a total pressure of $2.0 \times 10^{-3}$ mbar and an axial magnetic field of 436 G. The ion current is independent of discharge frequency and the bias voltage. The ion current is related to plasma density

![Fig. 1 — Cross-section view of microwave plasma beam system. M1: mass flow controller – nitrogen, M2: mass flow controller – hydrogen, S: negatively biased sample for surface treatment, Q: quartz window, A: coaxial antenna](image1)

![Fig. 2 — Ion current at the negatively biased sample](image2)
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( measured with the help of a langmuir probe) the profile of which is shown in Fig. 3. The plasma density is maximum at the center which is $1.1 \times 10^{12}$ cm$^{-3}$ for the above conditions and falls off to approximately $1 \times 10^{11}$ cm$^{-3}$ about 10 mm away from the center.

2.2 Nitriding experiment with high density plasma beam

A specially constructed austenitic SS201 sample was used for the nitriding experiment with high density plasma beam. For simplicity we will call this high density plasma beam as microwave plasma beam. The SS sample has diameter of 16 mm and height of 14 mm. Provision was made to insert a SS tube of 6 mm diameter with one end closed which also serves as the contact point for a K-type thermocouple’s junction. The SS tube serves as the sheath material for the thermocouple, one (closed) end of which is inside the vacuum chamber and the other (open) end is outside the vacuum chamber. Thus, the thermocouple assembly can be used to bias the SS201 sample in addition to monitor its temperature.

A mixture of nitrogen and hydrogen was used for the nitriding experiment. Mass flow controllers for the hydrogen and nitrogen gases were used to control the flow rates for 10 sccm and 5 sccm, respectively with a total pressure of $2.0 \times 10^{-3}$ mbar (measured by a capacitance manometer). Once the pressure got stabilized, plasma was created using the pulsed microwave power supply. We have used pulse frequency of 500 Hz with a duty cycle of 50%. A bias voltage of –380 V was used to get to the process temperature of 400°C. It took approximately half an hour to get to the process temperature starting from room temperature. After it reached the process temperature, the sample was treated for one hour and then plasma beam was switched off.

2.3 Nitriding experiment with glow discharge

For a comparative study, a SS201 sample was treated with conventional dc glow discharge plasma for 3 h at 530°C using the same mixture ratio of hydrogen and nitrogen, i.e. 2:1 and a total pressure of 2.0 mbar.

3 Results

3.1 Microhardness analysis

Small sections of the nitrided samples were cut transversely with low speed precision diamond cutter for microstructural investigation. The cut sections were put in mold materials using a mounting press. Thereafter, the mounts were ground and polished with the help of an automatic grinder/polisher.

Figure 4 shows the cross-section view of the nitrided layer of the surface treated by microwave plasma beam. The gray colour of the nitrided layer is clearly visible after nital etching. The thickness of the nitrided layer is 26 microns and is uniform throughout the surface. The microhardness profile is shown in Fig. 5. The microhardness was measured to be 1884 HV at 9 micron, 1019 HV at 24 micron and 334 HV...
far from the surface (core hardness). Thus more than 5 times increase in surface hardness was achieved by microwave plasma beam nitriding for only one hour of treatment at 400°C which also provides a case depth of 26 microns.

Microhardness measurements were also made on the surface after gently polishing it with 2000 grit SiC paper to make it look shining as it looked prior to the nitriding process in order to facilitate viewing of the indents of the diamond indenter. Measurements were made at nine different locations uniformly distributed throughout the surface of the sample (Table 1).

The microhardness values show uniformity throughout the surface with the average value being 1969 HV. All the measurements are within ±10% of the average value which are also the uncertainty limits of measurement.

Figure 6 shows load dependent test results of surface hardness for three samples, one untreated, second surface treated by glow discharge plasma nitriding (GDPN) at 530°C for three hours and third surface treated by microwave plasma beam nitriding (MPBN) at 400°C for one hour. The untreated sample shows a surface hardness of 341 HV irrespective of load (on the diamond indenter). The GDPN treated sample, however, provides ~1500 HV for 10 and 20 g load. Thereafter, it drops considerably. The cross-sectional measurements show only a depth of 10 microns for the nitrided layer if 1000 HV is taken as the lower limit. The MPBN treated sample shows a very high surface hardness of 1990 HV for 10 and 20 g loads and drops only marginally even with a high load of 200 g.

3.2 X ray diffraction analysis

X-ray diffraction patterns for the untreated, GDPN treated and MPBN treated are shown in Fig. 7(a and b) for “powder mode” as well as “glancing angle mode”, respectively. The “powder mode” spectra clearly show that the untreated sample is austenitic in nature. This is also confirmed by bringing a powerful rare earth magnet close to it which showed no effect on it. However, grinding and polishing mechanism does change the surface a little bit in the sense that magnet does move the sample a bit but the force is not enough to lift even the small sample. The glancing angle (2°) XRD spectra [Fig 7(b)] showed magnetic (ferrite) “α” phases in addition to non-magnetic (austenite) “γ” phases.

The glancing angle XRD spectra for GDPN and MPBN treated samples showed complete absence of “γ” phases implying the processes have transformed the “γ” phases to “α” phases. This was confirmed by bringing the rare earth magnet close to treated surfaces. It could lift the GDPN treated sample on touching the surface. However, the strongest effect was observed for the MPBN treated sample as it could lift it even from a distance of one centimeter away from the surface. The XRD patterns showed formation of nitrides for the treated samples. Most of
the peaks are common to CrN, Cr$_2$N, Fe$_3$N and Fe$_4$N. However, our microhardness measurements would indicate that rather high hardness of 1990 HV could be due to conversion of high percentage of chromium to chromium nitride$^{12,13}$.

While it (chromium nitride precipitates) was expected$^{14,15}$ for the GDPN sample (treated at 530°C), its formation at low temperature of 400°C for the MPBN treated sample seems to imply that if the ion flux impinging on the surface is very high it could convert Cr to CrN, Cr$_2$N rather efficiently at 400°C.

4 Discussion

Earlier research works indicated that it was possible to nitride austenitic stainless steels such as SS304 at low temperatures in the range 350-450°C with the help of high density plasma sources such as ECR and PSII. In order to investigate this effect even further, it was envisaged to develop even more dense plasma source so that the ion current density on the surface for treatment can be increased an order higher. Present plasma source which we call for simplicity as microwave plasma beam nitriding (MPBN) source provides a current density of 30 mA/cm$^2$ compared to 1-2 mA/cm$^2$ obtained in the glow discharge plasma nitriding (GDPN) process. For comparison, we list below the values (as reported in the literature) of plasma density for various plasma sources used for plasma based nitriding of steel surfaces:

GDPN: plasma density close to the cathode surface (surface for treatment) $\sim 1\times10^{10}$ cm$^{-3}$
PSII: plasma density close to the cathode surface (surface for treatment) $\sim 1\times10^{10}$ cm$^{-3}$
ECR: plasma density close to the surface for treatment $\sim 2\times10^{11}$ cm$^{-3}$
MPBN (present work): plasma density close to the surface for treatment $\sim 1\times10^{12}$ cm$^{-3}$

It has been shown that GDPN is not very efficient in nitriding at low temperature$^{16}$, i.e. below 500°C. ECR and PSII can nitride at low temperatures, i.e. 350-450°C but provide only shallow case depths of few microns (maximum 10 microns) and maximum surface hardness of 1500 HV. The present work involving MPBN which provides much higher plasma density than ECR and PSII can nitride at low temperatures, e.g. 400°C and provide high case depth (26 microns with only one hour of treatment) and a very high surface hardness of 1990 HV not obtained with any other source previously.

In conclusion, the present work strongly suggests a relation of the efficiency of the nitriding process with plasma density, i.e. more the plasma density more efficient the nitriding process is specially at low temperatures.

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References