Enhancement of Surface Properties of Maraging Steel C300 by PlasmaNitriding

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Abstract- **Plasma nitriding of maraging stainless steel C300 was carried out at 450^{0}C, 470^{0}C, 490^{0}C, and 500^{0}C for 4 hours using a mixture ratio of N_2:H_2 = 1:4. The modified surface was evaluated for micro-hardness and characterized by optical microscopy and XRD. Corrosion tests were also performed on untreated and plasma nitrided samples. Various properties, such as microhardness, case depth, and corrosion resistance were investigated for both un-nitrided and ion-nitrided materials. The increase in surface hardness is by a factor of two for 450ºC and 470ºC while it is more than by a factor of three for 490ºC as well as 500ºC.**

As for the case depths it varied from 10 microns (µm) for 450ºC to as high as 90 microns for 500ºC. Optical microscopy confirms results obtained from micro-hardness measurements vis-à-vis thicknesses of the nitrided layers. XRD results also show formation of predominantly γ' (Fe_4N) phases at the surface at all temperatures, however its depth increases with temperature. Corrosion rates evaluated in an electrochemical cell in 3.5% NaCl indicate increase in its value at 450ºC processing temperature, thereafter it decreases compared to the untreated case. The best result is obtained for the case of 500ºC processing temperature.

Keywords—Maraging steel C300, plasma nitriding, microhardness, optical microscopy , XRD, elctrochemical corrosion

I. INTRODUCTION

Nitriding has been successfully employed to modify surfaces of various engineering materials to improve their metallurgical and mechanical properties. It is a chemical treatment used to enhance the performance in terms of fatigue and wear resistance of very highly stressed mechanical components. There are different types of nitriding methods based on the type of medium used. The treatment which is based on plasma, namely plasma nitriding [1] offers the following advantages: no environmental pollution, low gas and energy consumption, short treatment time, and high nitrogen potential.

Because of its advantages, plasma nitiriding technique is increasingly being used specially for steel materials which are otherwise hard to nitride using conventional techniques. One such type falls under the category namely maraging steels [2-10]. It is a kind of steel which has high strength, toughness and good ductility. Moreover it has 16% to 19% nickel which makes it highly corrosion resistant and resistant to scaling even at elevated temperatures. Because of these special properties it is widely used in aerospace industry and other niche areas.

The amounts of carbon content and other harmful elements in these steels are very low. However, when maraging steels are subjected to age treatment process a large number of very small (nano-sized) particles form within their grains which causes substantial improvement in their hardness and strength [11].

Among other properties, maraging steels exhibit excellent strength to toughness ratio, good machinability and weldability and ease of heat treatment. The highest alloy containing maraging steels consist of 18% of nickel and high percentage of cobalt. Alloys with high titanium and molybdenum contents combine strength values up to 2400 MPa with fracture toughness (K_{IC}) around 70 MPa [12]. Hardening treatment involves a solution annealing step in order to obtain a homogeneous martensitic matrix followed by an aging process at around 500°C for 1-4 hours. The Ni_3Ti phase is formed during the first step which is expressed as $(Ni, Fe, Co)_3$ (Ti, Mo) – followed by Fe_2Mo–$(Fe, Co, Ni)_2$ (Ti, Mo) [13-15].

The present investigation concerns a type of maraging steel, i.e. C300 which has hardly been studied for surface modification even though it has important applications [16]. The aim of the study is to find optimum temperature for improved surface hardness for wear resistance and also corrosion resistance.

II. EXPERIMENTAL

A. Material and treatments

The maraging steel C300 is high nickel and cobalt containing grade of steel, produced by vacuum arc remelting process. C300 is usually supplied in annealed condition where the microstructure consists of fine grained martensites [17,18]. This structure is then maraged (precipitation hardened) to achieve final properties employing a relatively low temperature that results in the required combination of high strength and toughness. Maraging steels are usually machined in the annealed condition [19].

The maraging steel C300 used for the present investigation has the following chemical composition (wt%): 0.0200% C, 0.0190% Si , 0.0340% Mn, 0.0040% S, 0.007% P, 18.4300% Ni, 4.8900% Mo, 0.0580% Al , 8.400% Co, 0.6300% Ti and balance Fe. Samples are of cylindrical shape of 10 mm diameter and 8 mm thickness. They were mirror polished using SiC abrasive papers of different grit size together with a disc polishing machine. The samples were cleaned thoroughly with petroleum ether to remove all impurities prior to plasma nitriding. Plasma nitriding was carried out in a DC glow discharge reactor using a mixture of H_2 and N_2 (4:1) at a total pressure of 5 mbar together with process temperatures of 450^0C, 470^0C, 490^0C, and 500^0C for a fixed duration of 4 hours. Temperature was continuously monitored using a K-type thermocouple and controlled by adjusting the bias voltage on the cathode (sample).

B. *Experimental procedure for plasma nitriding:*

Following procedure was followed for surface treatment by plasma nitriding:

(i) Loading of the sample:

- Open the plasma nitriding chamber.
- Load the sample in to the chamber and then close the chamber.
- Start the rotary pump followed by switching on the pressure gauge. A vacuum is created in the chamber by the rotary pump and monitored using a pressure gauge. After about 30 minutes of operation, pressure drops to 1.5 x10^{-2} mbar starting from atmospheric pressure, i.e. 1000 mbar.

(ii) Hydrogen flushing

- Hydrogen gas from gas cylinder is introduced in to the chamber for flushing out the impurities from the vacuum chamber. Mass flow controller is used to control the flow of hydrogen gas as per our requirement (48 sccm). The chamber is flushed for one hour.

(iii) Hydrogen plasma cleaning:

- DC voltage is applied between anode and cathode which ionizes hydrogen gas and forms positively charged hydrogen ions. These ions attract towards cathode and impinge on the cathode surface which in turn cleans the surface of the sample. During this process violet coloured glow discharge is observed. This cleaning step also removes the protective oxide layer formed on the metal surface so we get the totally exposed metal surface. Cleaning of all samples was carried out at 250-300°C for duration of 10 minutes.

(iv) Plasma nitriding:

- In the fourth step both hydrogen and nitrogen are allowed to flow into the chamber at predetermined rates (48 sccm and 12 sccm, respectively) and ratio (4:1). Nitrogen containing ions are created due to ionization processes which then get accelerated due to high electric field near the cathode and impinge on it (the metal surface). These ions diffuse into the metal surface and form a hard and wear resistant layer of nitride on the surface. A blue-violet coloured glow is observed during plasma nitriding. Fig. 1 shows a schematic of the experimental setup.

(v) Cooling:

- After the end of the treatment, the plasma is switched off while the flowing gases (nitrogen and hydrogen) carry the heat out of the chamber. Cooling time is around 30 minutes. Once the substrate temperature is below 40°C, the chamber is opened and the sample is taken out.

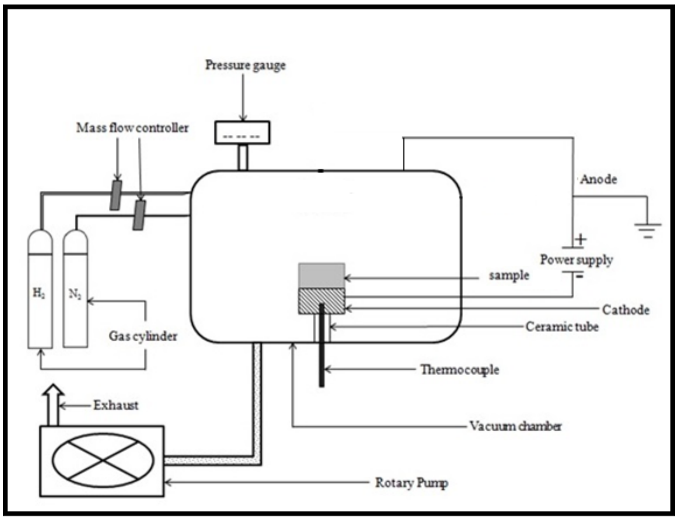

Fig 1. Schematic of the experimental setup for glow discharge plasma nitriding

III. RESULTS AND DISCUSSION

A. *XRD for phase analysis*

We analyzed the phase composition of the nitrided layers by XRD using Cu-Kα radiation. The XRD diffraction patterns are shown in figure 2. It can be clearly observed that sharp α' (Fe) peaks appear for the untreated sample. The α' peaks disappear for samples after nitriding at 450^0C and 470^0C but reappear at low levels when nitriding is carried out at 490^0C and 500^0C. Moreover, figure 2 shows formation of γ' (Fe_4N) phase for all the nitrided surfaces although relative heights of the peaks for the different crystallographic structures vary for the different processing temperatures. Because of high percentage of hydrogen used in the nitrogen-hydrogen mixture ε nitrides ($Fe_{2\text{-}3}N$) are not formed as confirmed by the XRD patterns.

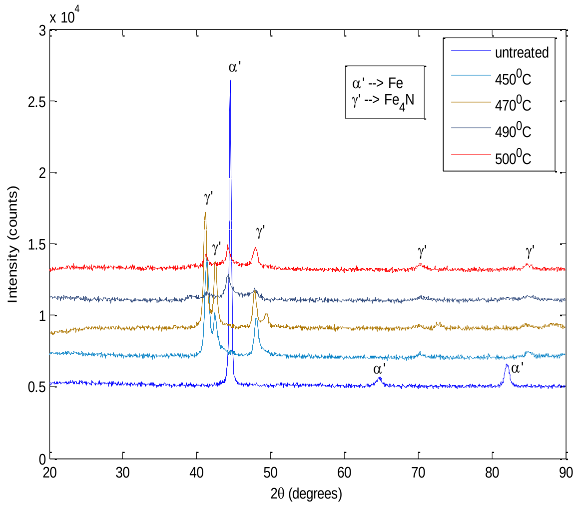

Fig 2. XRD patterns of surfaces of plasma nitrided samples

B. Corrosion behaviour of plasma nitrided verus untreated

Corrosion behavior was studied for the plasma nitrided samples as well as the untreated one in 3.5% NaCl solution using linear sweep voltammetry (log I vs. Volt) in an electrochemical cell. The Tafel plots were obtained which provided the corrosion rates. At lower temperature (450°C) the corrosion resistance deceases, but as the process temperature is increased corrosion resistance improves probably due to formation of thicker layers of Fe_4N, presence of which has been confirmed by X-ray diffraction analysis and this phase is known to be corrosion-resistant.

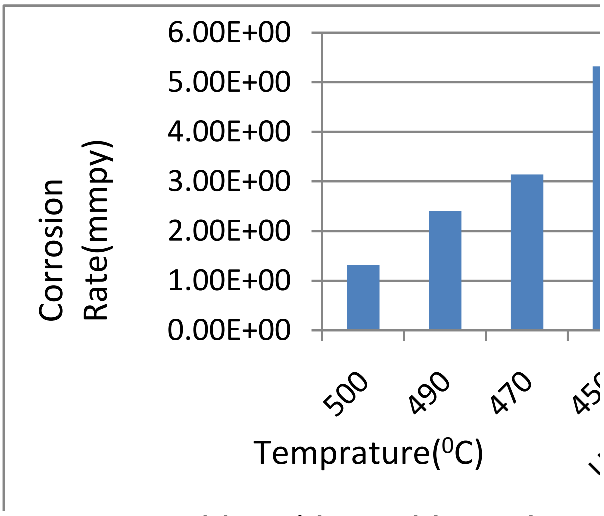

Fig.3. Corrosion behavior of plasma nitrided C300 steel

C. Microhardness measurements of cross section of the nitrided surface

Micro-hardness of untreated maraging steel C300 steel is 348 HV in annealed condition and after age hardening its hardness is increased up to 562 HV. The surface hardness after plasma nitriding goes up to 700 HV for 450°C and 470°C, however much higher (in excess of 1100 HV) for 490°C and 500°C. The best micro-hardness profile seems to be at the nitriding temperature of 490°C since microhardness is more than observed for other cases up to 100 microns. Fig. 4 shows the comparison.

Explanation for higher hardness obtained for the case of 490°C as compared to 500°C is attributed to different types of nitrides formed in the two cases as observed in optical microstructures (see section D). Determining the various phases formed as a function of depth from surface using appropriate characterization techniques is not within the scope of the present study.

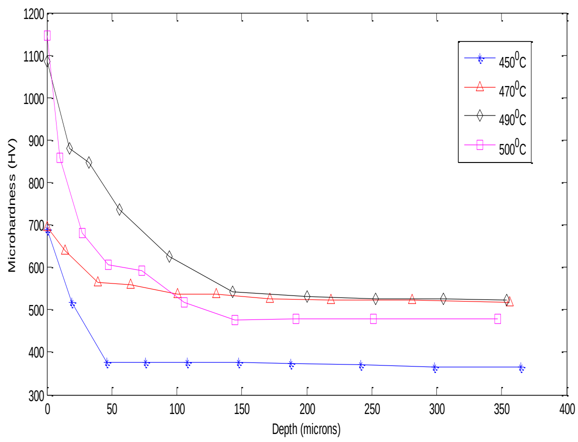

Fig.4. Microhardness profiles of plasma nitrided samples

D. Optical microscopy of cross section of the nitrided surface

Fig. 5 shows optical images (100x) of nital etched plasma nitrided samples. From the microstructure, the thickness of the nitrided layer can be measured. It is seen that at low temperatures, i.e. 450°C and 470°C nitrided layers are somewhat uneven, slightly thicker at edges compared to middle regions. Typically layer thickness was about 10 microns at 450°C and about 25 microns at 470°C. Layers are not dense which may explain why surface hardness has increased only by a factor of two (700 HV compared to untreated hardness of 348 HV).

At higher temperatures, i.e. 490°C and 500°C thicker (80 to 100 microns) and denser as well as uniform nitrided layers are observed (figures 5(c) and 5(d)). It is observed that the composition of the nitrided layer at 490°C (figure 5(c)) is different when compared with that of 500°C (figure 5(d)). While it (nital etched surface) is whitish in nature throughout the nitrided layer for the 490°C case, it whitish at the top (10 micron thick) followed by darker layer of 80 micron for 500°C when compared with bulk material. This may explain why microhardness profiles are somewhat different even though in both cases we obtain thick (80 to 90 microns) nitrided layers. It is also observed that bulk hardness for 500°C is about 50 HV less compared to those for 470°C and 490°C which may imply that annealing is taking place to some degree at this temperature.

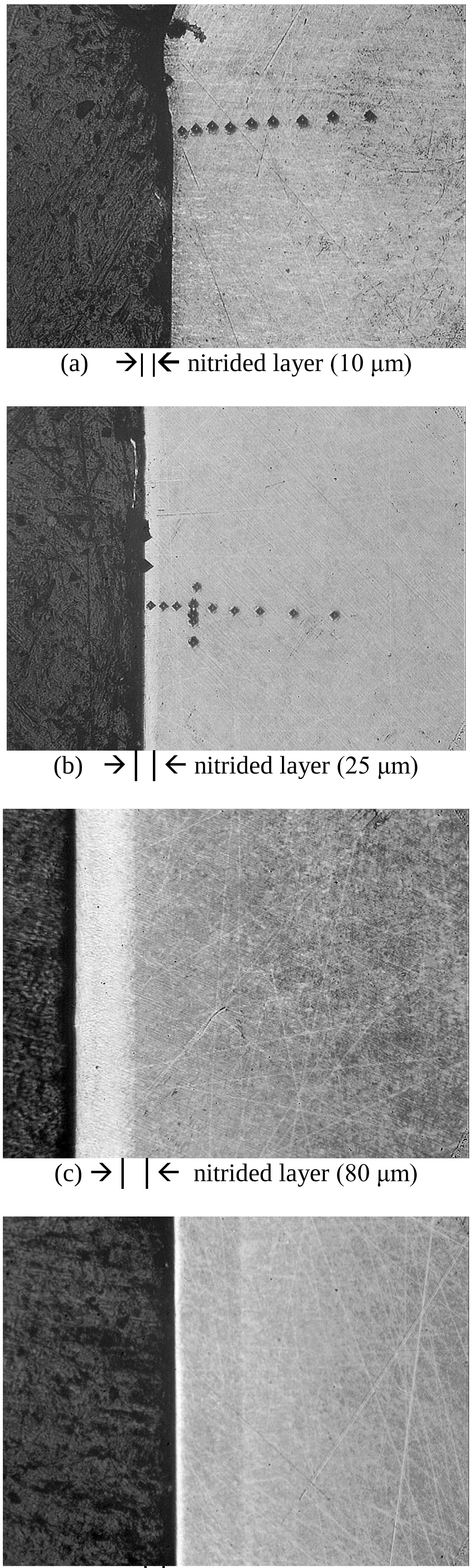

Fig.5. Optical images (100x) of cross sections showing nitrided layers for processing temperatures (a) 450ºC (b) 470ºC (c) 490ºC and (d) 500ºC

IV. CONCLUSIONS

The results of the present investigation involving plasma nitriding of maraging steel C300 at treatment temperatures of 450ºC, 470ºC, 490ºC and 500ºC using fixed nitrogen to hydrogen ratio of 1:4 can be summarized as follows:

- XRD analysis shows formation of γ'(Fe_4N) at all processing temperatures, however peak heights are different indicating different crystal structures (in relative terms) of Fe_4N are formed at different temperatures.
- Microhardness of the surface has increased by a factor of two for 450ºC and 470ºC and by more than a factor of three for 490ºC and 500ºC. The best microhardness profile is obtained for 490ºC treatment temperature. It also reveals case depths of 10 microns, 25 microns, 80 microns and 90 microns for 450ºC, 470ºC, 490ºC and 500ºC, respectively.
- Corrosion tests performed in an electrochemical cell in 3.5% NaCl solution yield best results at the highest treatment temperature, i.e. 500ºC. Initially corrosion rate deteriorates going from untreated to 450ºC, thereafter it improves steadily as temperature is increased to 500ºC.
- Optical microstructures of cross-sections of nitrided surfaces confirm microhardness profiles obtained for different temperatures, vis-à-vis thicknesses of the nitrided layers. Moreover, the microstructures of the nitrided layers for treatment temperatures of 490ºC and 500ºC look different implying hard compounds formed inside the nitrided layers are different in some respects as far as chemical composition is concerned although thicknesses of the nitrided layers are about the same (80 to 90 microns). This is in agreement with microhardness profiles which look somewhat different for the two cases.

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