1. Introduction

Plasma nitriding has become a powerful surface modification technique over other methods owing to several advantages.\(^1\) This technique produces less warping and distortion and offers increased resistance to wear, corrosion and fatigue. It also allows low substrate temperature treatment and avoids handling of hazardous and toxic chemicals. Recently plasma nitriding of chromium plated type 316 stainless steels has gained importance as it offers properties superior to nitrided type 316 stainless steel.\(^2\) Though electroplated chromium offers high hardness, corrosion resistance and low coefficient of friction, there are limitations in the applications of electroplated coatings. The microcracks developed during electroplating reduce wear and corrosion resistance. Besides, the hardness decreases significantly with increasing temperature above 623 K.\(^3\) In order to overcome these disadvantages, the surface of the electroplated chromium is modified by means of plasma nitriding. Chromium nitride coatings exhibit excellent thermal stability, wear and corrosion resistance and have been recently found as an alternative to titanium nitride coatings in tribological applications.\(^4\) Though nitriding behaviour of Fe–Cr alloys\(^5\) and austenitic stainless steels\(^6,7\) have been reported, plasma nitriding behaviour of chromium is very scarce.\(^2,3\) However, the conventional plasma nitriding that uses dc power supply encounters a limitation such as the formation of undesirable cathodic arc when intricate geometries or surfaces with protrusions or oxide phases are treated. This is largely overcome with the pulsed dc power supply which can operate in the frequency range 5–20 kHz. It is possible to apply a very fine dosing of input plasma energy into the workload, good temperature uniformity on the work piece with different geometries and homogeneous treatment even into small holes and slots. The use of pulsed sources enables the temperature of the specimen to be controlled by varying the width of the pulse without changing the bias voltage significantly. It has also been reported that the pulse width affects the microstructure and mechanical properties of the nitrided layers.\(^9,10\)

In this paper, the pulsed plasma nitriding behaviour of chromium plated type 316LN austenitic stainless steel is investigated. The influence of nitriding temperature, time and gas mixture ratio of nitrogen to hydrogen on the nitriding behaviour of chromium plated type 316 stainless steel has been investigated. The results indicated that the nitriding temperature plays a dominant role in obtaining hardness and case depth in this material. Plasma nitriding at a temperature of about 833 K produced a case depth of about 5 μm and surface hardness of about 550 HV. At temperatures more than 1 073 K, a large fraction of chromium has been found to be converted to chromium nitride with hardness exceeding 1 000 HV. Nitriding at an intermediate temperature of 913 K for 45 h has been found to produce nitrided layer of optimum properties. Calculation of diffusion co-efficients and activation energy for nitrogen diffusion are presented to demonstrate that the nitride layer growth in chromium plated stainless steel is a diffusion controlled process.

KEY WORDS: pulsed plasma nitriding; type 316LN stainless steel; chromium plating; diffusion.

2. Experimental

Type 316LN stainless steel samples of dimensions 100 mm×60 mm×10 mm were chromium plated by a private vendor. The coupons were given heat treatment at about 510 K for 3 h to avoid hydrogen embrittlement problem. The coatings in the as deposited condition at room temperature had hardness of about 850–900 HV at a load of
100 g. The chromium plated samples were ultrasonically cleaned in acetone and then loaded onto the cathode plate of the nitriding chamber. Pulsed plasma nitriding was carried out in an indigenously developed pulsed plasma nitriding facility. A schematic of a plasma nitriding system is shown in Fig. 1. The system essentially consists of a vacuum chamber, pumping system, pulsed DC power supply (900 V, 20 A, 1–20 kHz with variable duty cycle), mass flow controllers and temperature controller. The pressure control, voltage control and temperature control were performed through a personal computer interfaced with the nitriding facility. Prior to plasma nitriding, sputter cleaning was conducted in an argon atmosphere at a pressure of about 2 mbar by biasing the samples negatively (500 V pulsed DC) at 523 K for 2 h. Subsequently, plasma nitriding was performed at 3–5 mBar of nitrogen and hydrogen gas mixture in the ratio 4:1 or 3:1 at a desired temperature for various durations of time. To study the nitriding behaviour of the chromium plated stainless steel samples, the parameters such as nitriding temperature and time were varied. The flow rates of nitrogen and hydrogen were monitored using mass flow controllers and the temperature was controlled by varying the pulse to pause duration and hence the ion current at constant voltage. In order to suppress the arc formation during nitriding, the pulse length is usually kept shorter than the development time of an arc (≈100 μs). An auxiliary heater was used to nitride the sample at temperatures above 773 K. X-ray diffraction (XRD), scanning electron microscopy (SEM) and microhardness tester were used to characterize the nitrided samples.

### 3. Results and Discussion

The plasma nitriding of the samples was carried out for various durations in the temperature range 833–1 273 K. XRD analysis of the samples indicated the presence of hexagonal Cr₂N phase in the Cr matrix (Fig. 2). The intensity of the Cr₂N diffraction lines was found to increase with increase in the nitriding temperature owing to the increase in thickness of Cr₂N layer with temperature. The presence of untreated chromium was also observed below the surface layer of nitrides. Moreover, no traces of carbides and oxides were observed within the detectable limits of XRD. It is interesting to note that the nitrides were Cr₂N type and not CrN which were reported in the plasma nitrided type 316 stainless steel. The formation of Cr₂N was found to be more dominant in preference to CrN at an intermediate temperature (≈900 K) and high temperature (873 K<T<1 273 K) of nitriding of pure chromium. Surface morphology of the nitrided samples showed featureless structure with a random distribution of nitride particles (Fig. 3). Also the surface was found to be etched due to the ionic bombardment of nitrogen and hydrogen ions. A typical cross-sectional SEM microstructure of a sample of plasma nitrided chromium plated stainless steel at 913 K, 45 h is shown in Fig. 4. It is seen that the nitrided layer is uniform and the layer boundary is parallel to the sample surface, clearly indicative of a planar growth front. Figure 4 also shows the indentation marks due to hardness measurements by a Vickers diamond pyramid indenter. The sizes of the indentation marks show a gradual decrease in size as a function...
of distance from the matrix to the nitrided layer. The hardness–depth profiles (Fig. 5) show a uniform decrease in hardness as a function of depth for the samples nitried at the intermediate temperature of 913 K for different durations. The sample nitried at 913 K, 45 h has a peak hardness of about 900 HV for a depth of about 10 μm, hardness plateau of about 700 HV for a depth of 60 μm and finally followed by a smoothly decreasing hardness profile. When the sample was nitried at 913 K, 30 h, both the hardness and case depth were found to decrease. In both the cases, the decrease in hardness across the chromium–stainless steel interface is not abrupt. In contrast, the hardness–depth profiles have a sharp variation at the interface for the samples nitried in the temperature range 1173–1273 K (Fig. 6). At these temperatures the nitriding reaction proceeds by the formation of a uniformly hard surface owing to increased reaction rates of chromium with nitrogen which advances progressively into the core. The form of hardness profile developed during the nitriding is known to depend upon the interaction between the nitride forming elements and nitrogen and upon ease of nucleation of a nitride phase. A similar sharp interface between the nitried case and the core has been reported in nitried austenitic stainless steel and Fe–Ti alloys. Also, Fig. 6 shows that the peak hardness reaches values close to 1800 HV. Study on thermal stability of CrN and Cr2N indicated that there was a decrease in hardness for CrN phase due to decomposition at temperature above 1100 K. Therefore, it is plausible to conclude that the high hardness obtained at these high temperatures of nitriding was due to the formation of Cr2N phase.

It must also be mentioned that the stability of chromium coating and stainless steel matrix when they were subjected to nitriding at various temperatures. The stability of these materials was monitored by measuring the surface hardness as a function of nitriding temperature (Fig. 7). For example, it is seen that at 823 K, the hardness decreases only very slightly for stainless steel, while it decreases by three times for chromium coating. However, the important advantage of the plasma nitriding even at this temperature was that the surface hardness has increased to about 850 HV due to the formation of chromium nitride phase.

The observed case depths, hardness and diffusion coefficient of nitrogen as function of nitriding temperature and time are shown in Table 1. It is noticed from the table that when the nitriding temperatures were less than 973 K, the case depths were very small and the hardness obtained were less than 900 HV and at temperatures more that 1073 K, there was a considerable increase in case depth and hardness exceeding 1400 HV. Based on the time of nitriding (t) and case depth (X), the diffusion coefficients of nitrogen (D) were calculated from the relation, $X^2 = 2Dt$. These values are shown in Table 1. Figure 8 is lnD versus 1/T plot.
indicating that the nitrided layer growth in chromium plating is a diffusion controlled process. The activation energy for nitrogen diffusion in chromium determined from the plot was found to be 131.4 kJ/mol. Previously, we have reported an activation energy of 69.4 kJ/mol for diffusion of nitrogen in the nitrided layer of type 316 austenitic stainless steel. It is interesting to note that the activation energy for nitrogen diffusion in chromium plated stainless steel is significantly higher than that of austenitic stainless steel. This causes a significant reduction in the nitrided layer formation in the Cr plated stainless steel when compared to austenitic stainless steels especially at low nitriding temperatures. It is suggested that the rate of diffusion of nitrogen has been further restricted due to the formation of hard impervious Cr$_2$N phase at the surface of the Cr plating.

4. Conclusions

The nitriding behaviour of plasma nitriding of Cr-plated stainless steel was investigated as a function of nitriding temperature and time. An activation energy of 131.4 kJ/mol for the diffusion of nitrogen in chromium suggested that the rate of nitriding in pure chromium was low and the formation of hard Cr$_2$N phase was found to retard the diffusion rates of nitrogen in Cr-plated austenitic stainless steel. A reasonable value of hardness of 550 HV was obtained when the nitriding temperature was about 833 K and it reached a maximum value of 1800 HV at 1273 K even for short duration of nitriding. Plasma nitriding at an intermediate temperature of about 900 K for about 45 h produced a peak hardness of about 900 HV with a uniform decrease in hardness as a function of depth. Nitriding at intermediate temperatures might produce hard surfaces with an excellent bonding with the matrix. The high hardness and stability of the chromium nitride even at 1273 K also offer a possibility to use this material as diffusion barrier coatings.

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