Diffusion Layer Growth Mechanism in ASPN Method Using an Iron Cage for St52 Steel

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Received: April 2016 Accepted: April 2017

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DOI: 10.22068/ijmse.14.2.24

Abstract: *The mechanism of diffusion layer growth in plasma nitrided coatings applied on a St52 steel using an active screen is investigated. The nitriding was performed at 450,500 and 550 ◦C temperature nitriding times of 5, 10 and 15 h, in a gas mixture containing 20 vol. % H2: 80 vol. % N2 and DC-pulsed plasma nitriding unit.*
The surface, cross section and the thickness of diffusion of specimens was studied in terms of optical and scanning electron microscopy. According to the measurements of diffusion layer thickness, values of Q and D0 for nitrogen diffusion in substrate were calculated as 50585 (j/mol) and 4.11× 10-10 (m2/s)respectively. The variations of depth of hardness during nitriding period was determined.

Keywords: *plasma nitriding, AISI St52 tool steel, Diffusion zone, Growth mechanism, microhardness, Active Screen*

1. INTRODUCTION

Plasma nitriding process enhanced by an active screen is commonly used to improve steels, titanium alloys, aluminum alloys, polymers and ceramics corrosion behaviour and wear resistance [1-3]. In this process, problems of conventional plasma nitriding like the edge effect is completely omitted since the plasma is produced on the screen and not directly on the surface of sample[4,5].

During the plasma nitriding process of steels, the nitriding reaction takes place on the surface and in subsurface of substrate[6,7]. As a result, two different structures have been identified, the so-called white or compound layer and the diffusion zone. The outermost layer is compound layer, and consists of one or two kind of iron nitrides (Fe4N–Fe2–3N), depending on the process parameters. Below the white layer nitrogen atoms diffuses toward substrate which produces a diffusion zone [8-10].

In diffusion zone, the diffusion thickness, d, is defined as the depth, can be estimated as [12, 13]:

$$d = (De.t)1/2 \qquad \text{(Eq.1)}$$

Where De is the effective diffusion coefficient which depends on the diffusion and trapping (nitride formation) of N. The constant c in Eq. (1) takes into account the onset time of the nitriding process, and t is the treatment time.

The temperature dependence of the effective diffusion coefficient (Dk) can be approximately expressed in an Arrhenius form [11,14]:

$$Dk = Dk0 \exp(-Qk/RT) \qquad \text{(Eq.2)}$$

where Dk0 is so-called pre-exponential factor, Qk the activation energy for diffusion, R=8.3144 (Jmol-1K-1) the ideal gas constant, and T the absolute temperature. With c coefficient and De in Eq. (1) Dk0 and Qk for the diffusion of nitrogen in diffusion layer could be calculate[15,16].

In this study, the kinetics of diffusion layer produced by active screen plasma nitriding method on A St52 steel was determined. The effect of nitriding time and temperature on composition, structure and thickness of the nitrided layer was investigated by XRD optical (OM) and scanning electron microscope (SEM). The topographical evolution and surface

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Table 1. Parameters related to screen and sample location

Screen Material	Screen diameter	Screen height	Screen hole diameter	Distance between screen holes	Distance between screen and sample edge	Distance between screen and sample
St 37	10 cm	10 cm	1 cm	1 cm	3 cm	7 cm

roughness were studied by atomic force microscopy (AFM). It was found that there is a correlation between these properties and nitriding of the samples.

2. EXPERIMENTAL PROCEDURE

A typical St52 boiler steel (chemical composition 0.27% C, 0.6% Mn, 0.18% Si, 0.2% Cr and 0.45% Cu, wt %) were used in this study. Chemical composition of steel was examined by quantometry analysis. Specimens were wire cut from the bars in the form of discs with 25 mm diameter and 10 mm height. All of the specimens were surface ground and polished using 60, 80, 120, 240, 400, 600, 800 and 1000 SiC grit and 0.5 μm alumina powder, respectively.

The polished specimens were placed on an insulated ceramic in an iron screen with 0.8 mm thickness, plasma nitrided in a pulsed DC plasma reactor. The plasma nitriding was performed with a 10 kHz frequency and 60% duty cycle at 450˚C, 500˚C and 550˚C for 5, 10 and 15 h. The process parameters used in the nitriding chamber are shown in Table 1.

X-ray diffraction (XRD) (Philips PW-1730), was used for phase composition analyze. VEGA II TESCAN scanning electron microscopy and optical microscopy (Carl-Zeiss, 4996387) used for cross sectional microstructure of coatings. Cross-sectional microhardness profiles were obtained on polished surfaces, using a Buehler microhardness tester equipped with a Vickers indenter applying 50g of load.

3. RESULTS AND DISCUSSION

The XRD patterns of the plasma nitrided samples treated at 450 ˚C, 500 ˚C and 550 ˚C for 10 h are shown in Fig. 1, which indicate that the compound layer consists of γ′ and ε iron nitrides. In general, increasing the treatment temperature resulted in an increase in the intensity of the γ′ and ε phases. This may be explained by the increase in the compound layer thickness for an increase in the treatment temperature. In fact at higher temperature more FexN particles would deposit from screen on the substrate surface

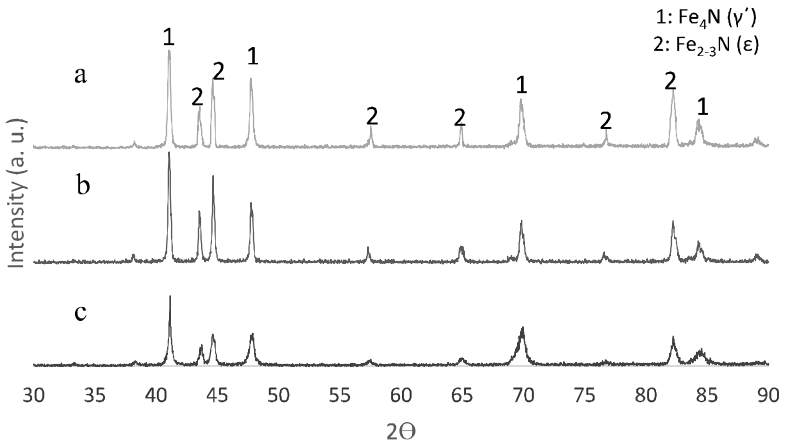

Fig.1. XRD patterns of active screen plasma nitrided samples for 10h and 450˚C (a), 500˚C (b) and 550˚C (c)

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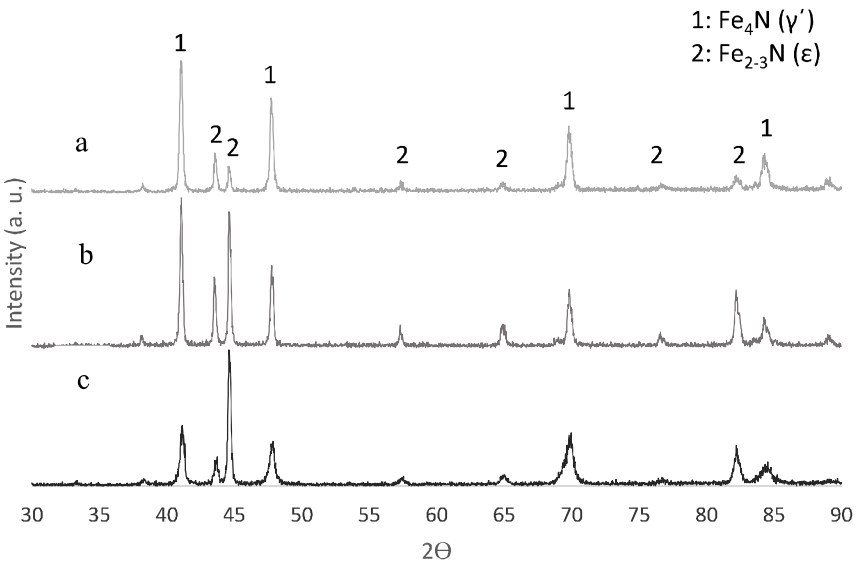

Fig. 2. XRD patterns of active screen plasma nitrided samples at 500˚C for 5h (a), 10h (b) and 15h (c)

which results more diffusion of nitrogen toward substrate. Fig. 2 shows effect of plasma nitriding time on iron nitrides peak intensity. It is clearly seen that intensity of γ′ phase increases due to decomposition of Fe2-3N to Fe4N at longer treatment time.

The sample cross-section after plasma nitriding using an active screen at a gas mixture of 20 % H2: 80 % N2 and a temperature of 500 ˚C for 10 h is presented in Fig. 3. A diffusion zone and compound layer present on the surface can be seen. Fig. 4 shows the results of the compound layer thickness as a function of treatment temperatures. Increasing temperature causes thicker compound layer. Growth of the compound layer is controlled by diffusion of nitrogen through this layer [17]. At low treatment temperature the diffusion coefficient of nitrogen atoms is low, therefore the compound layer and diffusion layer are thin. Increasing treatment temperature results in an increase in the nitrogen diffusivity, leading to the formation of thicker layers.

Thickness of layers assessed using OM and SEM cross sectional images are in Fig. 5. It is seen that by increasing the coating time, the thickness of the layers increases which is due to the growth of the iron nitride particles descending from the top screen. Similar results have been reported by other researchers [18]. One of the important properties of active screen plasma nitriding method is Enhancement of the coating

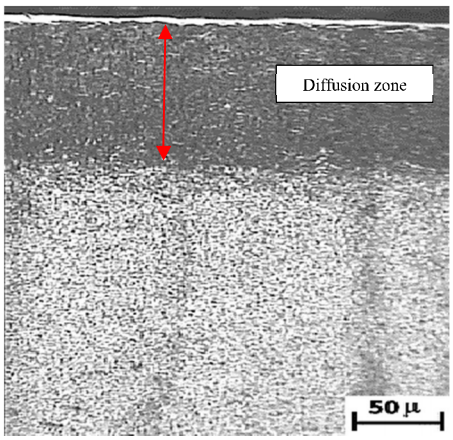

Fig. 3. Optical micrograph of typical specimen plasma nitrided at a gas mixture of 20 % H2: 80 % N2 at 500 ◦C for 10 h.

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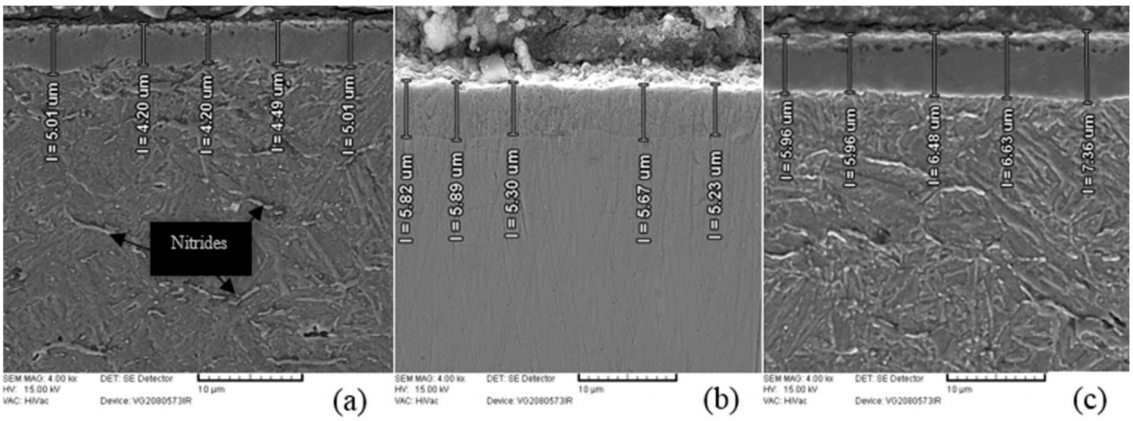

Fig. 4. SEM secondary electrons micrographs of the cross section specimen plasma nitrided at a gas mixture of 20 % H2: 80 % N2 at 450˚C, 500 ˚C and 550 ˚C for 10 h.

thickness with nitriding time [1]. In conventional plasma nitriding, prolongation of time would decrease the thickness of coating due to the direct formation of the plasma on the surface of the specimen and continuous surface sputtering whereas in ASPN process the plasma forms on the screen. Thus, particles deposit continual on the surface leading to increase in coating thickness by treatment time. Moreover, thickness of layers is depended on temperature by Arrhenius equation [19]. In fact, increasing temperature causes increment in diffusion constant which produces thicker diffusion zone.

Cross sectional microhardness depth profile of samples nitrided at different nitriding time in 450˚C, 500 ˚C and 550 ˚C is illustrated in Fig. 6 (a-c). The results clearly show that near surface hardness is higher by 3 times compared to that of un-nitrided substrate material. Surface hardening induced by nitriding, can be attributed to the [20]; Solution of nitrogen atoms in the iron lattice which induces solid solution strengthening,

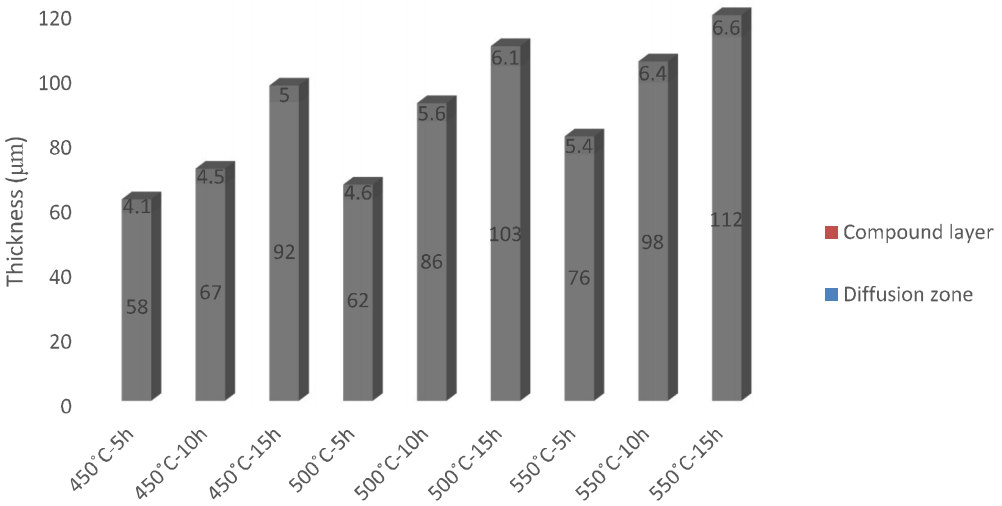

Fig. 5. Thickness of compound layer and diffusion zone for nitrided samples at various plasma nitriding condition

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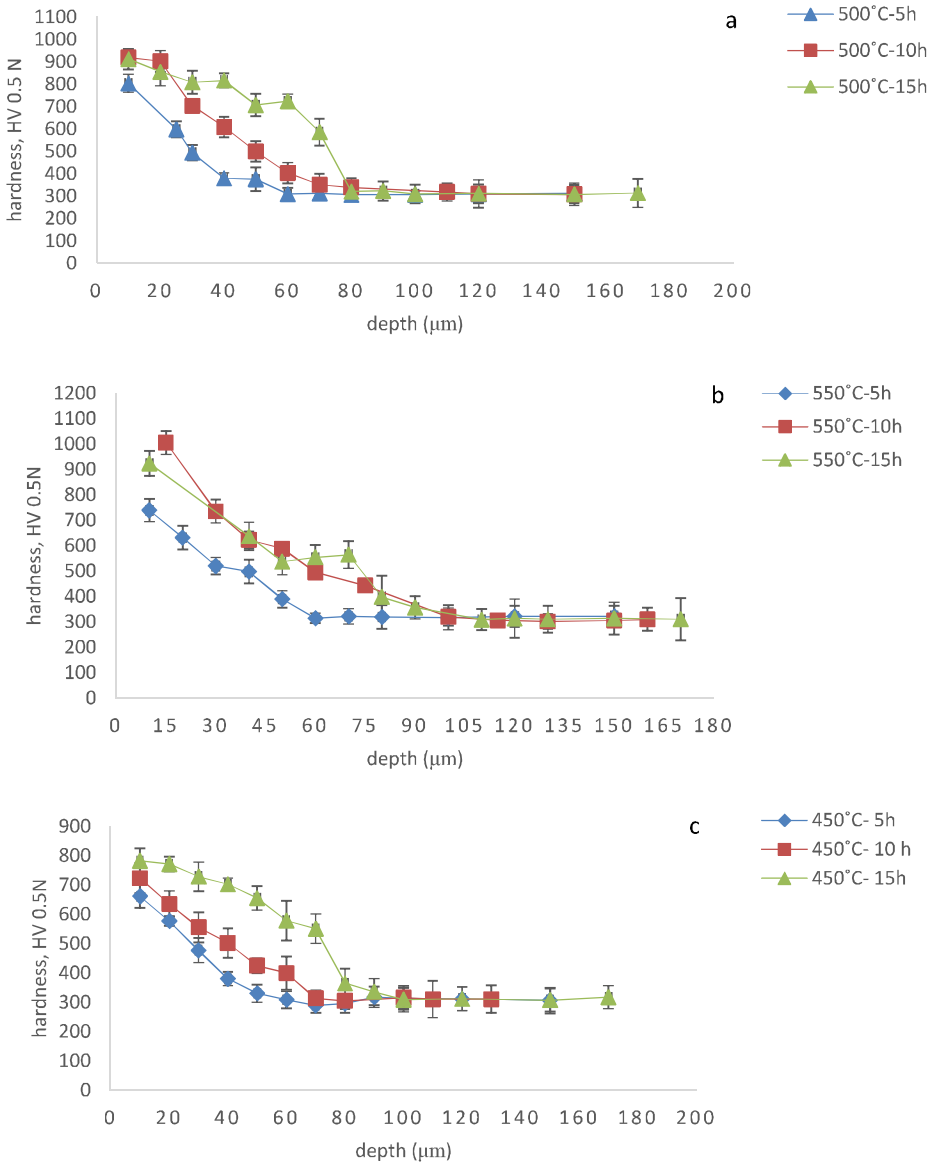

Fig. 6. Cross-sectional hardness-depth profile after plasma nitriding for different time at (a) 450˚C, (b) 500˚C, (c) 550˚C

formation of alloy nitrides and fine precipitates acting as obstacle against dislocations movement and development of compressive residual stress as a result of structural misfit because of formation of interstitial solid solution and alloying element nitrides. Moreover, Fig. 6 shows that at longer times, more atomic nitrogen diffuses from top surface towards substrate and hence expanding diffusion zone. Incremental decline in top surface microhardness could be due to the growth and coarsening of nitride precipitates which leads to lower precipitate density and lower hardness [15, 21]. Diffusion depth and microhardness is enhanced by temperature at different treatment times. Higher temperature could increase the driving force of atomic nitrogen diffusion toward the substrate which may induce nitrided phase in a higher depth.

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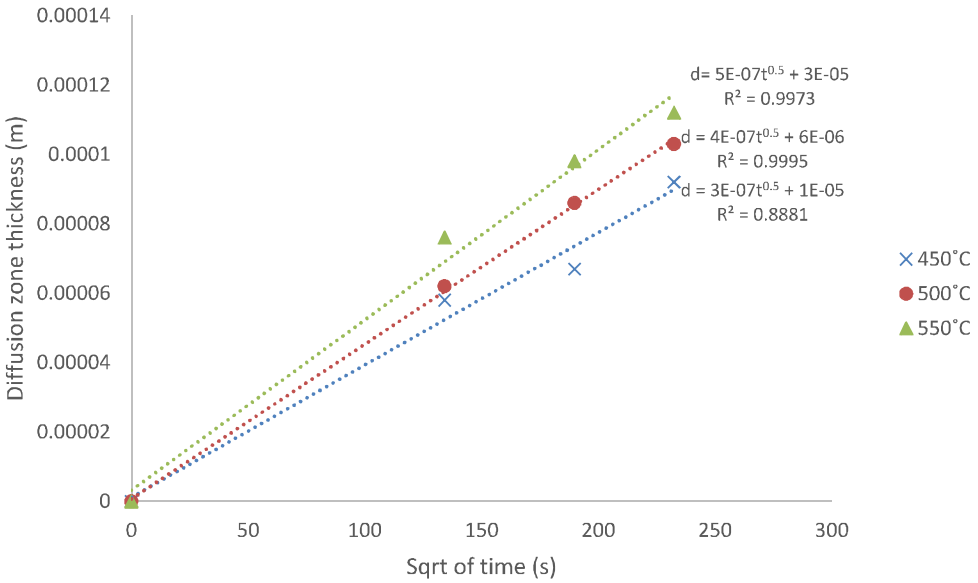

Fig. 7. Diffusion layer thickness as a function of plasma nitriding time

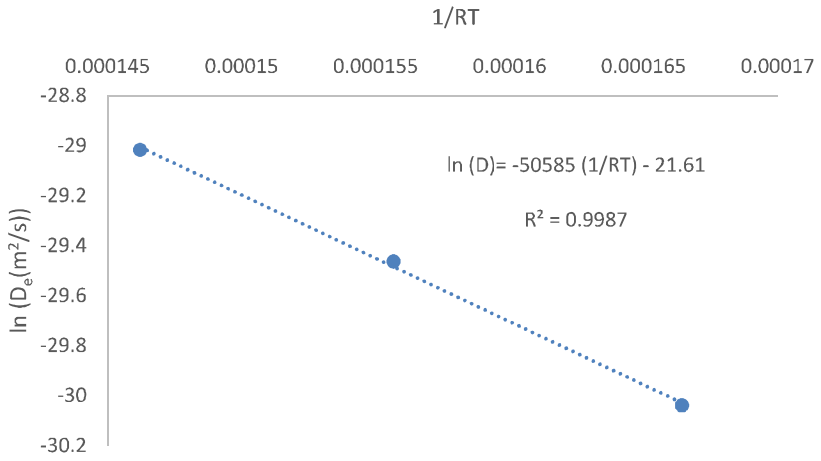

Fig. 8. Calculated values of Q and Dko for nitrogen diffusion in substrate.

In Fig. 7 the variation of diffusion depth estimated by OM, SEM and microhardness depth profile is drawn versus the nitriding time. A linear relationship was found between d and t0.5 as expected for a diffusion controlled process. The symbols represent the obtained results and the curves are obtained from fitting of Eq.1 on obtained results. Regarding the results of diffusion thickness measurements and with the usage of Arrhenius equation Eq. 2, values of Q and Do for nitrogen diffusion in substrate were calculated as 50585(j/mol) and 4.11×10^{-10} (m^2/s), respectively. Diffusion coefficient of nitrogen (Dn) at 450˚C would be calculated 3.7×10^{-13} (m^2/s) by substituting Q and Do values in Eq. 2. 3.7×10^{-13}. Fig. 8 shows values of Q and Dko for

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nitrogen diffusion in substrate.

4. CONCLUSION

The compositions of the coatings were studied by X-ray diffraction technique. The results showed that the compound layer was consisted mostly of dual phase -Fe4N and -Fe2–3N. Increasing treatment temperature increased both -Fe4N and -Fe2–3N in the compound layer, however increasing the processing time increased only the -Fe4N phase. Increasing treatment time and temperature increased both the compound and diffusion layer thicknesses. A linear relationship was found between the diffusion layer depth and the square root of the nitriding time, as expected for a diffusion controlled process. Values of Q and Do for nitrogen diffusion in substrate for ASPN method were calculated as 50585(j/mol) and 4.11×10^{-10} (m^2/s), respectively.

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