Nitrogen diffusion in different microstructures of plasma nitrided CK45 steel

F. Foadian*1, F. Feyzi2, S. Haghighat3 and H. Aghajani4

In this study, the nitrogen diffusion in different microstructures of CK45 steel was studied. Different microstructures were achieved by different heat treatment cycles as annealing, normalising and quench tempering. After heat treatment, plasma nitriding was performed at 550°C temperature, nitriding times of 5 h, in a gas mixture containing 25 vol.-%H2/75 vol.-%N2 and DC pulsed plasma nitriding unit. The surface, cross-section and the thickness of diffusion and white layers of specimens were studied in terms of optical and scanning electron microscopy. Surface phases have been studied by X-ray diffraction analysis. Results showed that by normalising the samples, higher diffusion depths could be achieved and the white layer thickness would be also higher. Other results showed that core hardness of quench tempered specimens could decrease after plasma nitriding due to being subjected to nitriding process temperature.

Keywords: Plasma nitriding, CK45 steel, Diffusion zone, Compound layer, Microstructure, Hardness

Introduction

Surface modification studies of high quality steels, like AISI 1045, is of great fundamental and technological interest.1–4 By changing surface properties of industrial steel parts, it is possible to increase their resistance to applied stresses, considerably. One of the ways to obtain high complex surface physical and mechanical properties of metallic materials is a thermochemical heat treatment method, known as nitriding.5 Although, it is possible to nitride many steel grades, high surface hardness is usually obtained when special nitriding steels containing aluminium, chromium, molybdenum or vanadium alloying elements are used. These elements form hard and stable nitrides as soon as they come into contact with nitrogen atoms diffusing from the surface to the core of the workpiece. Studies show that nitriding of plain carbon steels would result only moderate hardness.6

Plasma nitriding is a well known method for surface hardening of nitridable metals.7–9 This method is one of the most effective techniques for increasing wear resistance,10,11 fatigue strength,12 surface hardness and corrosion resistance of industrial components.13–17 In addition, it is an environmentally clean process, among its many beneficial features.18–21 The process was developed in the early 1930s by Egan and Berghaus as an alternative to the gas nitriding process.22 It is a thermochemical process involving diffusion of atomic nitrogen into the surface of target materials to form hard nitrides of the metal alloying elements in the steel. In the plasma nitriding process, the target material is continuously subjected to a flux of ions present within a glow discharge.23 In this process, usually, components are placed on the cathode of an electrical circuit while the chamber walls become the anode. By applying a certain voltage between anode and cathode, a glow discharge region is formed all over the cathode surface. In this glow discharge, the components become heated through the transfer of energy associated with the action of ionic bombardment. As a result, nitrogen is transferred to the workpieces and then diffuses into the surface where it forms nitride precipitations in the steel. This leads to formation at the classical nitrided structure, with a surface compound layer and a diffusion zone supporting it.24 Compound layer can consist of iron nitride phases, γ prime, Fe3N or epsilon, Fe2–3N.25 Since it is unaffected by acid etching and remains white, it referred white layer too. The corrosion properties of non-alloy and low alloy steels are improved by the thin white layer of iron nitrides.23 Below the compound layer, there is a diffusion zone where the steel matrix is supersaturated by nitrogen atoms. The diffusion zone with its induced compressive residual stresses enhances fatigue strength of the workpiece.26 The nitriding temperature is usually below 590°C, which is under eutectoid temperature in Fe–N diagram.7

AISI 1045 steel is within the class of medium carbon content steels. Presence of carbon increases steel hardness and tensile strength. Owing to these, as well as other physical and chemical properties, the AISI 1045 steel can be used for component parts in machinery, automotive and allied industries (hydraulic shafts, motor shafts, axles and gears). Carbon steels also have considerable applications in nuclear technology, e.g.
piping systems, low and high pressure turbine sections and reactor vessels.\textsuperscript{26,27}

In this work, AISI 1045 steel were annealed, normalised, quenched and tempered in different temperatures, and the effects of these microstructures on diffusion of nitrogen were studied.

**Experimental**

**Specimen preparation**

The standard chemical composition of 1045 steel is Fe–0.44\%C–0.25\%Si–0.66\%Mn–0.015\%P–0.049\%Cr–0.017\%Mo–0.058\%Ni–0.008\%Al–0.25\%Cu (wt\%). Disc type specimens, 2 cm in diameter and 1 cm in height, were cut from a bar with a diameter of 5 cm. The specimens were manually ground to 1000 grit to achieve a fine finish and then polished with alumina powder (1 μm). Etching was done with 3% nitral.

**Heat treatment**

In this work, quenching in brine and tempering, annealing and normalising treatments were selected for heat treatment of specimens. In normalising treatment, the specimens were heated from room temperature up to 900°C and kept at this temperature for 10 min, then were air cooled. In annealing, the specimens were heated from room temperature up to 850°C and kept at this temperature for 10 min, then were cooled in powered off furnace. In quenching, the specimens were heated from room temperature up to 835°C and kept at this temperature for 10 min, then were quenched in brine.

As quenched specimens were studied in four conditions, untempered and after tempering in 450, 500 and 550°C. For tempering, specimens were heated up to mentioned temperatures and kept at these temperatures for an hour and then were cooled in air. The time and temperature for each heat treatment process were selected according to the continuous cooling transformation diagram of the steel.

In order to identify the microstructures, all specimens were polished again then etched with nital solution.

**Plasma nitriding**

After heat treatment, plasma nitriding was carried out using a direct pulsed current in a semi-industrial scale unit. Specimens were heated up to desired temperature by plasma. Nitrogen and hydrogen gases were used to supply system’s gas. To start the process of plasma nitriding, the pressure inside the chamber was reduced to a value up to 10\(^{-5}\) atm, and surface of \(\text{H}_2\) specimens was cleaned under hydrogen atmosphere by sputtering process for 30 min.

Plasma nitriding was carried out in a 75\%\text{N}_2+25\%\text{H}_2 atmosphere at a temperature of 550°C for 5 h. Nitriding time was calculated when the specimens reached to desired temperature within 2 h. After nitriding, the system was turned off, and the pressure of the chamber reduced to 10\(^{-5}\) atm, and specimens were cooled inside the chamber by spending about 3 h time. After cooling, the microstructure of the specimens was characterised with an X-ray diffraction (XRD) analyser, optical metallography and scanning electron microscopy (SEM). In addition, surface hardness of the nitrided specimens was obtained using Vickers hardness tester.

**Results and discussion**

Table 1 lists the hardness of the all specimens before and after nitriding. Before nitriding, macrohardness of specimens was measured. After nitriding, microhardness of specimens was measured using 0.1 N forces. The results of hardness before nitriding indicate that the minimum values are related to annealed specimens and the min and max values correspond to annealed and as quenched samples, respectively. In addition, it can be seen that by increasing the tempering temperature of as quenched specimens, the hardness is reduced, so that by tempering at 550°C, the hardness is equal to the hardness of normalised specimen. Moreover, the results indicate that, except as quenched specimens, nitriding treatment increases the surface hardness of all other samples. Reduction in hardness is due to specimen tempering, so it can be concluded that, increasing of hardness by nitrogen could not compensate the reduction of hardness, caused by tempering.

The XRD patterns of the nitrided specimens indicate that the surface of all specimens contains \(\gamma'\)(\text{Fe}_4\text{N}) and \(\alpha\text{(Fe}_{2–3}\text{N})\). Figure 1 shows XRD results of as received specimens at nitriding.

Figure 2 shows the microstructure of reference specimen before and after nitriding. Microstructure of reference specimen consists of a ferritic matrix with pearlitic grains. According to \(\alpha\) high nitrogen diffusion coefficient compared to pearlite phase, it is possible to change nitrogen diffusion by changing these two phases.
a microstructure of reference specimens before nitriding and b depth of nitride layer in reference specimen

3 Images (SEM) of nitrided samples

a reference; b normalised at 900 C; c–e annealed at 900 C
Aghajani et al. studied the effect of grain boundary size on nitrogen diffusion. They concluded that applying heat treatment before nitriding has a significant effect on diffusion depth of nitrogen because the heat treatment influences on grain size and so diffusion paths. Diffusion depth could be changed by different heat treatment such as annealing and normalising. Smaller grain size for normalised specimens in comparison to annealed ones increases nitrogen diffusion. Figure 3 shows an SEM image of the surface of the reference specimen, before and after nitriding. Figure 3 indicates that diffusion of nitrogen breaks the pearlitic lamellas in areas close to the nitriding surface as well as forming nitride compounds in grain boundaries. Consequently, diffusion of more nitrogen has changed the morphology of pearlitic and cementite lamellas. In addition, it is possible that treatment in nitriding temperature may dissolve cementite, but because the nitriding temperature is much lower than the $A_{C3}$ temperature of the steel, the probability of dissolution is very low.

There is no obvious change in the microstructure of annealed and normalised specimens after nitriding. A significant change was observed in the structure of as Q and QT specimens. Figure 4 shows the images of QT specimen’s surface. It seems that coarsening of grains by tempering in nitriding temperature can be stopped by formation of nitride precipitates in grain boundaries. Consequently, much growth was not seen in the surface of grains. There is no evidence of grain growth near the surface of QT 450°C specimens, but in the zones far from the surface, the grains have been grown (5-a). This indicates that nitriding temperature has caused additional tempering in the specimens. The same happens is also happened in tempered samples at 550 and 550°C.

Figure 4b–e shows the depth of nitriding layer in the specimen which was quenched and tempered at 450, 500 and 550°C. In the annealing specimens, the depth of nitrogen diffusion in the grain boundaries was reduced due to coarsening of the grains in comparison with reference specimen. In normalised specimens, the optimum combination of grain size and density of grain boundaries was obtained. Thus, in these specimens, the diffusion of nitrogen could be limited via two mechanisms: bulk diffusion and grain boundary diffusion. Consequently, the depth of the nitrogen diffusion was reduced.
increased. In Q and QT specimens, the depth of diffusion is very low. In Q specimens, the amount of penetration is close to the annealed specimens.

Conclusions
From this work, the following conclusions are achieved.
1. Hardness of annealed specimen is lower than the other heat treated specimens. Hardness of quench tempered at 550°C specimen is almost same as normalised specimen.
2. After plasma nitriding of all specimens, ε and γ′ were formed on the surface of all specimens.
3. After plasma nitriding, all specimens’ hardness is increased. Since during the nitriding, in as quenched specimen tempered, hardness is decreased.
4. Nitrogen diffusion in tempered structure is more than Q structure and in Q structure is more than ferritic or pearlitic structures.

References