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RESEARCH ARTICLE

EVALUATION OF COATING PROPERTIES PRODUCED BY ELECTROLYTIC PLASMA NIT RIDING ON CK45 STEEL

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ABSTRACT

In this work, iron nitride coating produced on CK45 steel by electrolytic plasma nitriding was investigated. Two types of electrolytes were used: electrolyte (A); 2 g/L $Ca(NO_3)_2$ + 2 g/L NH_4NO_3 + 6 g/L Na_2CO_3 and electrolyte(B); 2 g/L NH_4NO_3 + 2 g/L $NaNO_3$ + 6 g/L Na_2CO_3. Structure analysis of the coating layers was investigated by X-ray diffractometer (XRD) and surface morphology by scanning electron microscopy (SEM). Corrosion resistance of samples in 3.5% NaCl solution was evaluated by anodic potentiodynamic polarization and Electrochemical Impedance Spectroscopy (EIS). Corrosion current density for the coating with electrolyte (A) was about 1.3 times lower than uncoated sample and corrosion current density for the coating produced by electrolyte (B) was 2 times lower than uncoated sample.Micro hardness test was also performedbyKoopadevice model MH3. Both coatings showed more micro hardness than that of uncoated sample.

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INTRODUCTION

Since steel hasa high strength, high toughness, suitable machining ability, low cost, and good availability, it has found a wide application in many industries (Luk *et al.,* 1998). However, corrosion resistance and wear resistance of steel are not as good as required, thus surface coating and surface treatment on steel has become an important exercise for an increase in work-piece lifespan, efficiency, and improvements of its economics (Luk *et al.,* 1998). Plasma electrolytic saturation (PES) recently was widely used for surface treatment of steel (Luk *et al.,* 1998; Yerokhin *et al.,* 1999; Luk *et al.,* 1999; Tsotsos *et al.,* 2002). In plasma electrolytic saturation treatment Samples were slowly immersed into the electrolyte, after that DC voltage was applied to the samples. On the surface of the sample, the hydrogen film which was formed rapidly with the surface temperature grew slowly. Sudden stable arc discharge is formed on the sample, and then the coating thickness increases with time. After PES treatment, samples were quenched in the solution to the room temperature by shutting down the power supply. After being quenched, the samples were removed from the clamping device and cleaned by ethanol alcohol. During recent years, many investigations about the PES of metals and alloys using light elements, preferably carbon and nitrogen, have been carried out (Kusmanov *et al.,* 2014). The basic focus of these studies was on the structural features produced by the coatings, composition of the phases, the hardness distribution of the layers, and the wear and corrosion resistance (Kusmanov *et al.,* 2014). The most important purpose of the nitridingis to improve the surface hardness, wear resistance and corrosion resistance, while the core of the nitrided parts can maintain high strength and toughness (Hua *et al.,* 2013). The workpiece placed in an electrolyte and subjected to arc discharge can obtain a very high hardness, wear and corrosion resistance in a few minutes. The features of the nitrided layer is mainly affected by process parameters which are voltage, processing duration, current density, frequency and electrolyte composition (Hua *et al.,* 2013). Most of the usual chemical heat treatment technologies for tribological applications up to the date have been based on high temperature created in a gas atmosphere chamber. These processes are expensive because they take place in a closed furnace for thermal diffusion treatments, and they cannot be used in production lines operating at room temperature and ambient pressure. This problem was solved in industries by using a new generation of plasma electrolytic saturation techniques, such as the plasma electrolytic nitrocarburizing and plasma electrolytic Nitriding (Jiang *et al.,* 2013). Plasma electrolysis nitriding (PEN) was a coating treatment used in order to improve the wear, corrosion and fatigue resistance of steels. The thickness and the composition of a coating layer depend on the type of chemical reactions occurring at the sample surface as well as the diffusivity of nitrogen in the treated material (Keddam, 2008). Nitriding has been used

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industrially for a long time and widely used to improve the wear resistance, corrosion resistance and the fatigue strength of ferrous material (Hashmi, 2014). All iron materials were nitridablebeginning with cast iron and unalloyed as well as low-alloyed steels to high-alloyed stainless steels and highalloyed powder-metallurgical processed tool-steels (Hashmi, 2014). Iron nitrides could be passivatedto show increased resistance against neutral salt solutions, atmospheric corrosion, and tribo-oxidation (Hashmi, 2014). Plasma electrolysis is cost-effective and increase of work-piece life (Shen *et al.,* 2007). In plasma electrolysis, saturation when sample is connected to the negative electrode (cathode) can forma ceramic coating on steel (Kumruogˇlua, 2010). The coating layer formed by the plasma electrolysis process is affected by several parameters such as type of the power source which affects the coating structure (Liu *et al.,* 2009; Lv *et al.,* 2008), frequency which is able to change the surface roughness and size of the pores (ASTM D4541-09e1, 2009).

Experimental procedures

MATERIALS AND METHODS

Ck45 is a low carbon steel with composition: C 0.45%, Si 0.21%, Mn 0.64% and Fe bulk. Samples were available in the two shapes and sizes: cylindrical with 30mm (diameter) × 5mm (height) and cubical with 30 × 20 × 5 mm. Nitriding was performed in aqueous medium with a nominalnitrogen containing chemical composition (such as NH_4NO_3), water and conductive agent. In this aqueous solution, electrolytic conductivity was attained by addition of Na_2CO_3. Nitrogen source was NH_4NO_3, $Ca(NO_3)_2$ and $NaNO_3$. Also electrolytes composition were: electrolyte (A) 2 g/L $Ca(NO_3)_2$ + 2 g/L NH_4NO_3 + 6 g/L Na_2CO_3 and electrolyte(B) 2 g/L NH_4NO_3 + 2 g/L $NaNO_3$ + 6 g/L Na_2CO_3. In plasma electrolysis saturation treatment samples were immersed slowly into the electrolyte, and then a 430V DC voltage was applied to the samples. On the surface of the sample, the hydrogen film rapidly formed with a gentle increase in the surface temperature. Time keeping starts when the sudden stable arc discharge is formed on the sample. Then, PES treatment samples in the solutionwere quenched to the room temperature by shutting down the power supply. Following quenching, the samples were removed from the clamping device and cleaned by ethanol alcohol. In Plasma electrolysis saturation sample connected to the negative electrical pole (cathode) and coating created on surface of sample. Also a metal was connected to the positive electrode (anode) that in this work was a stainless steel 316. The different phases present in the coatings were investigated with Philips-X'Pert X-ray diffractometer (XRD) (Cu Kα radiation). Surface morphology of the samples were investigated with SEM. The PEN treatments were carried out with equipment consisting of an electrolyte container, a DC pulse power supply, and a cooling system. PEN treatment conditions of the samples are presented in Table 1.

Table 1. sample parameters in PEN treatment. Electrolyte (A): 2 g/L $Ca(NO_3)_2$ + 2 g/L NH_4NO_3 + 6 g/L Na_2CO_3 and Electrolyte (B): 2 g/L NH_4NO_3 + 2 g/L $NaNO_3$ + 6 g/L Na_2CO_3

Electrolyte	Sample	Time (min)	Frequency (Hz)	Voltage (V)	Duty cycle(%)
A	AS1	10	5000	430	30
A	AS2	20	5000	430	30
B	BS1	10	5000	430	30
B	BS2	20	5000	430	30

Corrosion tests

Electrochemical tests such as anodic polarization (AP) and electrochemical impedance spectroscopy (EIS) were conducted on samples to determine its corrosion behaviors .In anodic polarization, samples were placed in three electrode cells containing saturated calomel electrode as reference electrode, platinum electrode as axillary electrode and sample as working electrode in solution of 3.5% NaCl. Before the onset of polarization, the potential of samples were monitored until the potential became stable and the polarization was started at -300 mv with respect to open circuit potential with a scanning rate of 1 mv per second until 400 mv .EIS was also done in three electrode cells. The amplitude of test was chosen to be 10 mv and the test was run in the range of 0.1 Hz to 100 kHz.T he results of polarization tests and EIS were analyzed to determine the corrosion resistance of the samples.

RESULTS AND DISCUSSION

Main phases

Two phases were detected by XRD on the coatings treated by PEN which were Fe and Fe_2N. Fe phase was austenite and after quenching in PEN treatment transformed tomartensite. Iron nitride (Fe_2N) coversthe sample surface. In electrolyte(A) and electrolyte(B) same phases were detectedas shown in Figures 1 and 2, iron nitride phase was created on the surface.

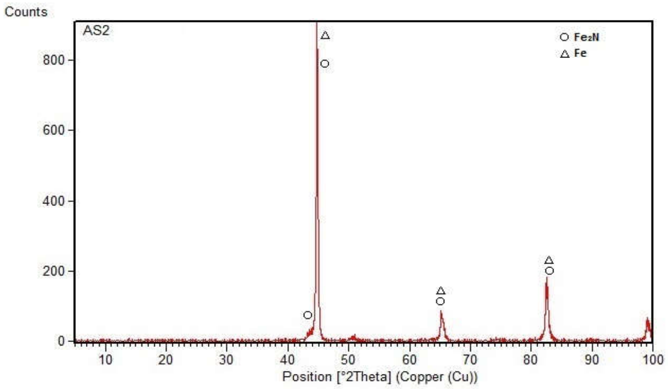

Figure 1. Phases in AS2

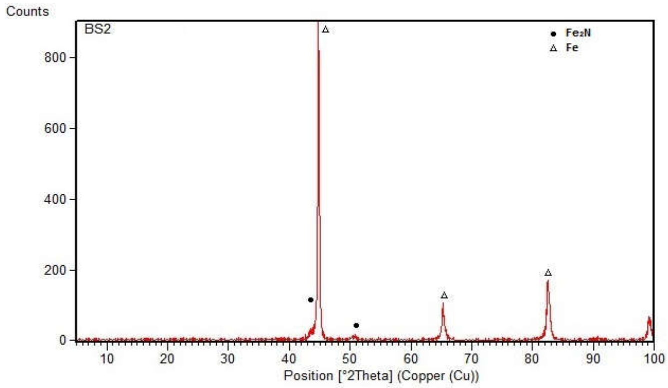

Figure 2. Phases in BS2

Morphology

The plain structure (iron nitride) was increased in AS2sample in comparison to That of AS1 as shown in Figure 3. Grainy structure was decreased in AS2 samplein comparison to that of AS1 sample. Iron nitride had uniform and plain structure. Substrate had grain like structure.

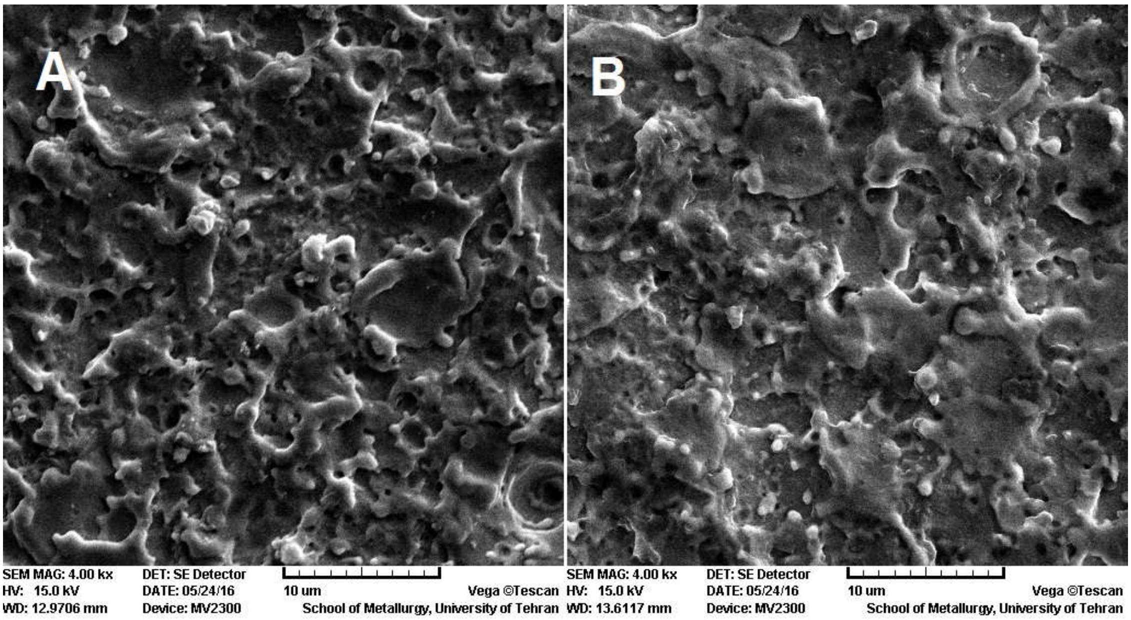

Fig. 3. SEM morphology, A) sample AS1 B) sample AS2

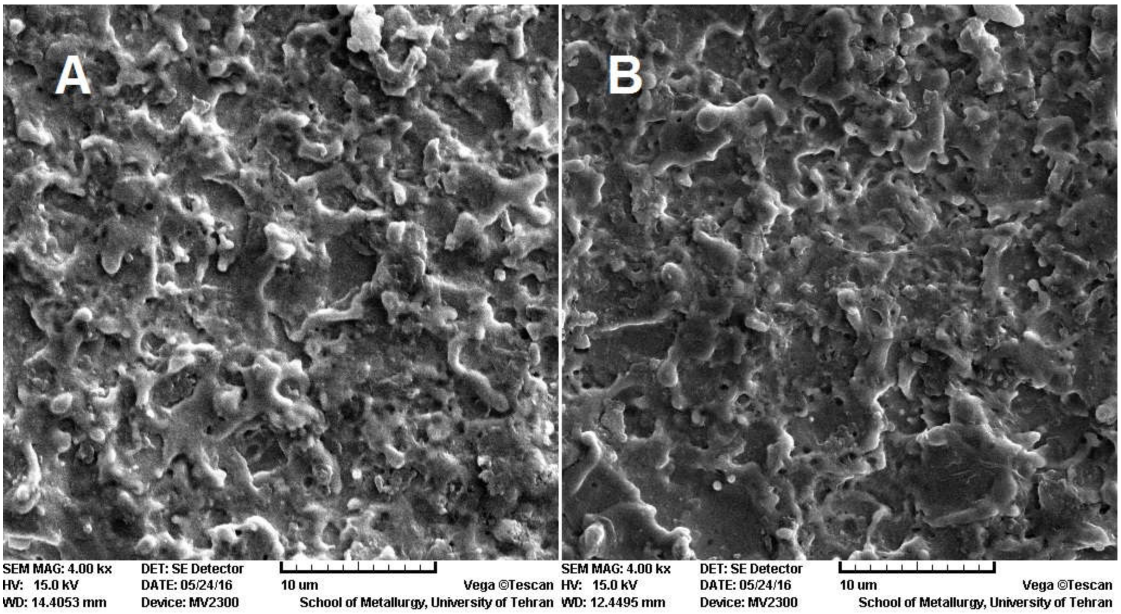

Fig. 4. SEM morphology: A) sample BS1 and B) sample BS2

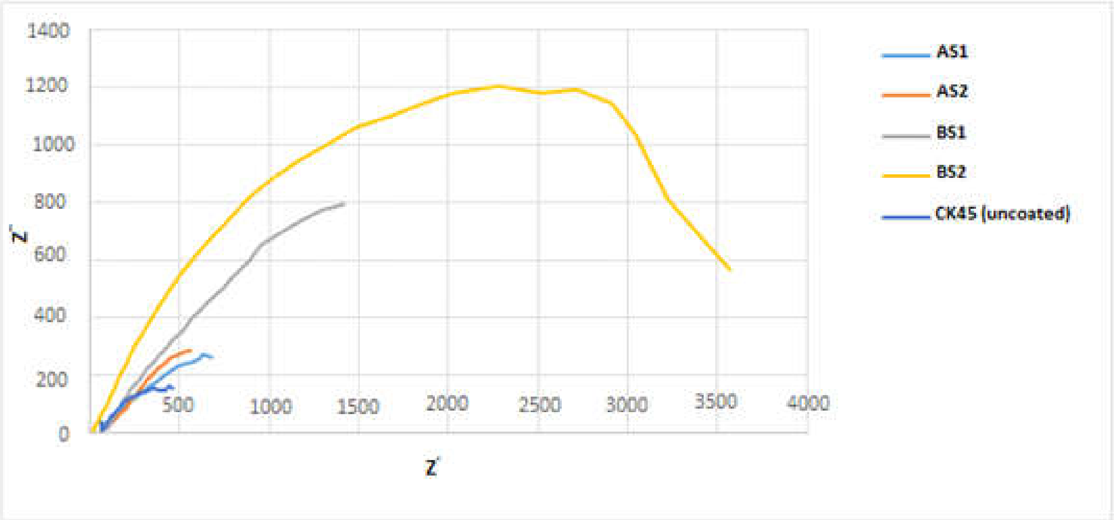

Fig. 5. Nyquist plot for CK45 uncoated and AS1, AS2, BS1 and BS2 coated samples

The plain structure (iron nitride) was increased in BS2 samplein comparison to that of BS1 sample as shown in Figure 4. The grainy structure was also decreased in BS2 sample in comparison to that of BS1 sample. Iron nitride and its substrate had a uniform and plain structure, and a grainy structure, respectively. This is observable in the section B of both Figures 3 and 4 where the plain structure is more dominant. Both electrolytes had the same surface structureandcreated the same coating. However, plain structure (iron nitride) was different in the samples.

Corrosion

The corrosion behavior of PEN coatings was analyzed with electrochemical tests. Corrosion resistance of samples in 3.5% NaCl solution was evaluated by anodic potentiodynamic polarization and Electrochemical Impedance Spectroscopy (EIS). Figure 5 shows theEIS results. This Figure also shows an increase in corrosion resistance with increasing PEN treatment time. Moreover, this Figure also shows the fact that allthe samples presented hadmore corrosion resistance thanthat of uncoated sample (CK45). Sample AS2 contained more iron nitride incomparison with Sample AS1; therefore, the formerpresentedmore corrosion resistance. Identically, Sample BS2 presented higher corrosion resistance due to the greater iron content. Figure 6 shows theanodic potentiodynamic polarization results. Samples AS2 and BS2 indicate lower current densities in comparison to that of uncoated sample CK45. This means that samples AS2 and BS2 may resist against corrosion more than that of the uncoated sample CK45. Corrosion current density of AS2 and BS2 was 1.47×10^{-4}(A/cm^2) and9.85×10^{-5}(A/cm^2), respectively. Considering the 1.89×10^{-4}(A/cm^2) corrosion current density of the uncoated CK45, AS2 and BS2 were1.3and 2 times more corrosion resistance than that of the uncoated CK45, respectively. In addition, the samples AS2 and BS2 showed a passive film on their surface which may resist corrosion while the uncoated sample did not show any passive film.

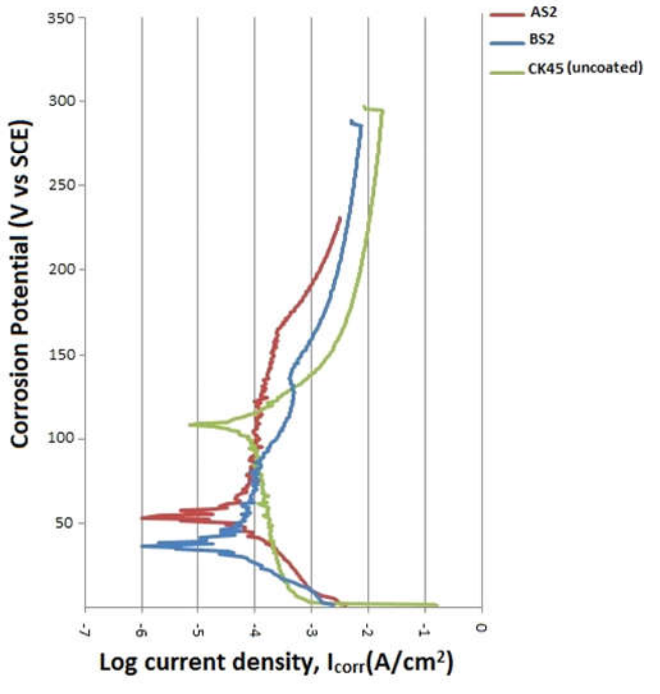

Fig. 6. Anodic Polarization curves for the substrate and samples AS2 and BS2 in 3.5% NaCl solution

Micro hardness

Table 2 showsVickers hardness for all samples. The micro hardness force and the force exertion time were 25 gr and 10 seconds, respectively. Iron nitride contentsincreased with increasing treatment timeas shown in Figures 3 and 4, this increase led to a decreasing in surface micro hardness. Identically, micro hardness of all PEN treated samples were higher than that of the uncoated CK45.

Table 2. Hardness of samples treated by PEN

Sample	AS1	AS2	BS1	BS2	CK45
Vickers hardness	559	458	453	363	200

Conclusion

Both electrolytes used for PEN treatment createda layer of iron nitride on sample surface. Longer PEN treatment times led togreater iron nitride contents andless micro hardness on the surface. Sample BS2 was more resistive against corrosion thanthat of the other samples. This means the coatings produced by electrolyte(B) had more corrosion resistancethan that of the coatings produced byelectrolyte(A). Corrosion current densitiesfor the samples AS2 and BS2 were1. 47×10^{-4} (A/cm^2) and 9.85×10^{-5}(A/cm^2), respectively. Considering 1.89×10^{-4}(A/cm^2) corrosion current density forthe uncoated CK45, samples AS2 and BS2 were 1.3 and 2 times more corrosion resistance than that of uncoated CK45, respectively.
Micro hardness created by 10 minutes of treatment time was greater than that of 20 minutes of treatment time. Thus more mechanical properties are obtainable in shorter treatment time. In comparison with those of the uncoated CK45, an increase in hardness may cause an improvement in mechanical properties (e.g. strength and toughness) formed by the coating (Aliofkhazraee *et al*., 2008). The authors declare that there is no conflict of interest regarding the publication of this paper.

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