

Plasma electrolytic surface carburizing and hardening of pure iron

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Abstract

In this study, surface carburizing of pure iron was investigated in aqueous solution, which consists of water, glycerin, and NH_4Cl , for a very short period of time. The formation of hard carbon-rich layer on the surface of pure iron was confirmed by XRD analysis. SEM study combined with EDS showed the presence of carbon in the coated layer. Moreover, RF-Glow Discharge Optical Emission Spectrometry (RFGDOES) presents only carbon diffusion into the base material. Metallographic and SEM studies revealed that a uniform and compact carbon-rich layer was firmly sticking to the surface of the pure iron, and there was no crack observed between a carburized layer and a substrate. The average thicknesses of carbon-saturated layers were changing from 12 μm for 10 s to 78 μm for 60 min. The hardness of the carbon-rich layer on the substrate was 850 HV, while the hardness of the substrate was 150 HV.

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1. Introduction

Carburizing is one of the most widely used surface hardening techniques for steel, mainly because it can offer the superior combinations of mechanical properties. The principles of case hardening were used centuries ago in the conversion of wrought iron to steel by the ‘cementation’ process. In general, during a carburizing process, low carbon steel containing 0.10–0.25% C is heated at elevated temperatures, usually in the temperature range of 900–1100 °C, in the presence of a carbon-rich medium. Carbon atoms diffuse into iron provided that the iron is in the FCC (γ) form above 910 °C and is held at that temperature long enough to produce a carbon-enriched layer of sufficient depth. Finally, carburized layer at the surface of the iron is produced. The carbon-rich layer or case can be subsequently hardened either by reheating and quenching, or by quenching directly from the carburizing temperature. Solid, liquid, and gaseous carburizing media can be used depending on the nature and scope of the work involved. The function of the carburizing

medium is to release atoms of carbon at the surface of the work piece so that, at the carburizing temperature, they will be absorbed interstitially into the steel [1–6].

Luk et al. used a method, called “electrolytic surface-hardening process,” as another way of surface hardening of medium or high carbon steel. The method is a special hardening process employing electrolysis in an aqueous solution under particular conditions. In this process, the work piece is connected to DC or pulse DC power supply as a cathode in an electrolysis cell. Once a stable hydrogen film is formed on the work piece by applied high voltage, then electrical discharge, including electrons and ion avalanche, occurs across the hydrogen film. Then, the work piece is heated violently to above the austenite temperature due to the generation of resistance heat under the applied voltage in a short time. Then, the hydrogen film around the work piece will break by shutting off the power of the electrolysis cell, and especially the surface of the work piece will self-quench and/or be quenched by the cold electrolyte surrounding the work piece, leading to hardening of the work piece [7].

The aqueous electrolyte surface hardening process has been used in the literature for surface hardening of medium or high carbon steels (AISI 1050) [7–10]. Plasma electrolysis for surface hardening by means of carburization, nitriding, or nitride/carbide formation on mild steel (0.4% C + 1% Cr) or

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low carbon steel (SAE 1020) and oxidation of aluminum alloys were studied extensively, and the review paper was published in the literature [11]. Moreover, plasma electrolytic nitrocarburising treatment for stainless steels was studied as well [12]. In addition, the mechanism of plasma formation was discussed in the literature [13]. However, plasma electrolytic surface carburizing of pure iron has not been reported hitherto in the literature. Application of this method on the pure iron and very low carbon steel (<0.1% C) is more important, and the method has potentially more wide applications in industry than those of the medium- or high-carbon steel. Therefore, this is a promising technique for the surface hardening of the pure iron.

In this work, the present paper reports on a study performed at 850 °C for 10 s, 30 s, 1 min, 2 min, 5 min, 10 min, 20 min, 30 min, and 60 min for the carburization of pure iron in aqueous solution, which consists of water, glycerin, and NH₄Cl by means of an electrolytic process. The purpose of this study was to investigate the carburization of the pure iron in aqueous solution by plasma electrolytic process.

2. Experimental procedure

2.1. Substrate materials

Substrate material used in this study was pure iron (99.97% weight) that had a shape of approximately 10 mm × 12 mm × 2 mm. All the samples were ground by 500 grit SiC paper and cleaned by ethyl alcohol before the plasma electrolytic surface carburizing treatment.

2.2. Plasma electrolytic carburizing system in aqueous solution

The schematic diagram of the plasma electrolytic surface carburizing treatment unit is shown in Fig. 1. The unit has a DC power supply which is capable of applying up to 300 V and 25 A. A sample is connected as a negative output and the stainless steel container is connected as a positive output of the power supply. The sample and thermocouple are attached to end of a non-conducting rod and moved by a stepper motor up and down (i.e., in and out of the solution). The stepper motor, sample holder assembly, and control units are not shown in Fig. 1. Solution was circulated by a pump and then collected in an over-flow tank. The heated solution is taken from the over-flow tank to a solution reservoir to cool down the solution to room temperature.

2.3. Plasma electrolytic surface carburizing

Carburizing was performed in an aqueous medium with a nominal chemical composition of 10 l of water, 1 kg of NH₄Cl, and 1 l of glycerin (C₃H₈O₃). The solution was prepared by solving first NH₄Cl in water and then glycerin

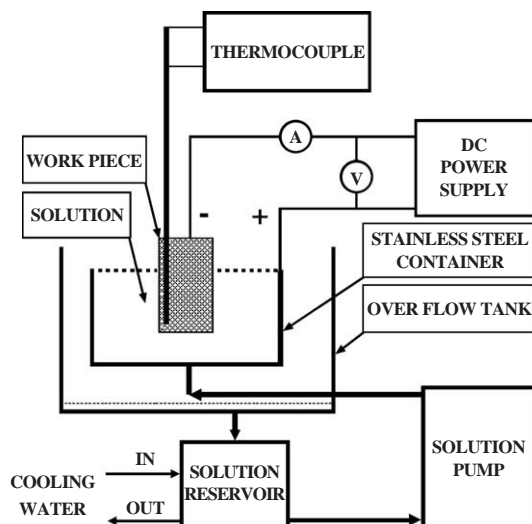


Fig. 1. Schematic representation of the plasma electrolytic surface carburizing system.

was added to the solution. In this aqueous solution, electrolytic conductivity was attained by addition of NH₄Cl, and glycerin acted as a carbon source. Temperature measurement of the sample was carried out using two thermocouples. The first one was attached to the surface of the sample and the second one was inserted into the sample approximately 1 mm to the surface by drilling a hole. The test material with thermocouples was mounted to a clamping device and was completely exposed to the electrolyte. After that, 210 V DC was applied to the sample and immersed slowly into the electrolyte by a step motor drive. In the vicinity of the sample, a gas film rapidly formed during the slow dipping process. The sample was heated up to 850 °C in a short time of 40 s due to the applied voltage and the resistance of the gas film formed at the surface of the sample. Once the surface temperature of the sample reached 850 °C for the applied voltage, the temperature remained stable. However, the measured surface temperature of the sample was 70 °C higher than the inside temperature, although inside temperature was not discussed in this paper. The samples were subjected to the carburization treatment in the same solution for 10 s, 30 s, 1 min, 2 min, 5 min, 10 min, 20 min, 30 min, and 60 min, and were quenched in the solution to room temperature by shutting down the power supplied. Following quenching, the samples were removed from the clamping device and cleaned by ethyl alcohol.

2.4. Microstructure characterization

Rigaku X-ray diffractometer (DMAX 2200) with a Cu K α radiation source of a wavelength of 1.541 Å over a 2 θ range from 40° to 90° was employed for the phase characterization of carburized layer of the samples. In addition, the presence of any preferred crystallographic orientation of the samples prior to the treatment was

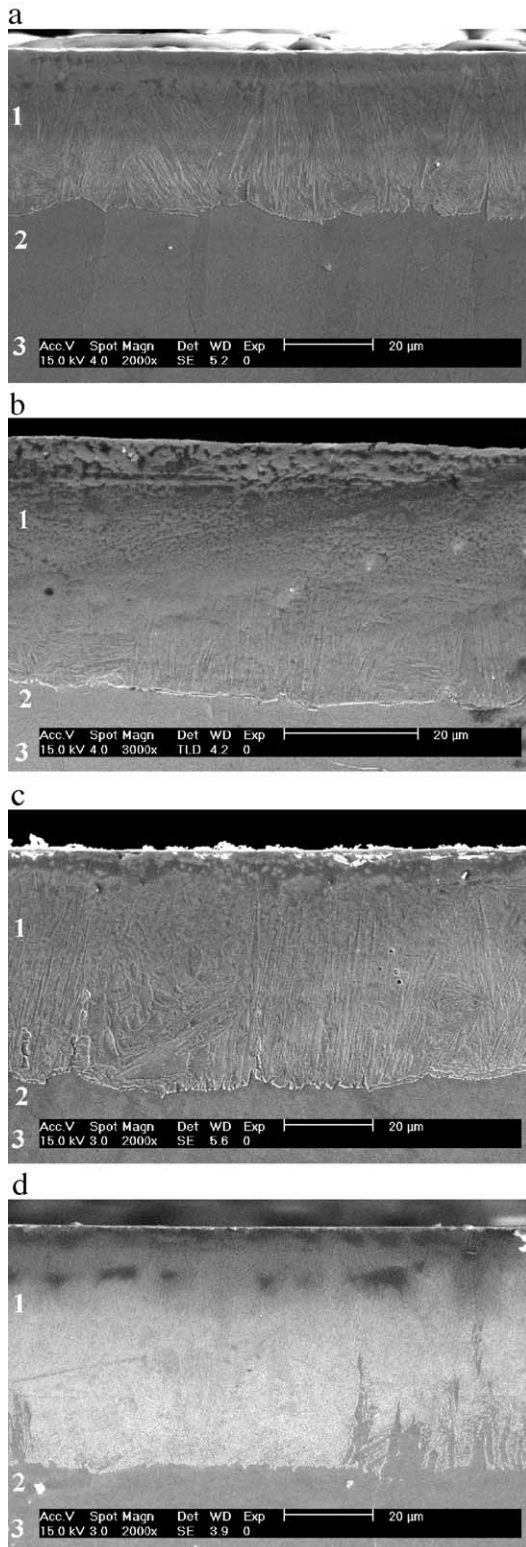


Fig. 2. (a) SEM image of pure iron carburized at 850 °C for 5 min, showing the carbon rich layer (1), the transition layer (2), and the base metal (3). (b) SEM image of pure iron carburized at 850 °C for 10 min, showing the carbon rich layer (1), the transition layer (2), and the base metal (3). (c) SEM image of pure iron carburized at 850 °C for 30 min, showing the carbon rich layer (1), the transition layer (2), and the base metal (3). (d) SEM image of pure iron carburized at 850 °C for 60 min, showing the carbon rich layer (1), the transition layer (2), and the base metal (3).

checked by $\theta-2\theta$ XRD scan; however, there was no preferred orientation observed before and after treatment. Samples for scanning electron microscopy examination were ground on wet emery paper down to 1200 grit and then polished by 1–3 μm diamond paste. Nital (3%) was used as etchant for a microstructural investigation. The microstructural examinations of the cross-section and the surface of the carburized layer of the sample were carried out by using Philips Field Emission Scanning Electron Microscope (FE-SEM). Thickness of carburized layer was measured under microscope.

2.5. Hardness measurement

Samples were cut perpendicular to the immersion direction using diamond saw and polished for microhardness measurement. The microhardness of carbon-rich layer formed on the surface of pure iron, and cross-sectional hardness variation from the surface of carburized layer to the interior of the sample was measured by a Instron microhardness tester equipped with a Vickers diamond indenter with a load of 100 g.

2.6. Study of surface elemental composition

The presence of possible elements in the coating was confirmed via energy dispersive X-ray spectroscopy (EDS). Depth profile analysis of the coated samples was qualitatively performed using RF-Glow Discharge Optical Emission Spectrometry (RFGDOES) (Jobin-Yvon Emission) equipped with a 4 mm diameter anode and operated at 45 W and 800 N/m^2 under argon atmosphere.

3. Experimental results

3.1. Microstructure

Scanning electron microscopy (SEM) examinations of carburized pure iron reveal compact and smooth coating.

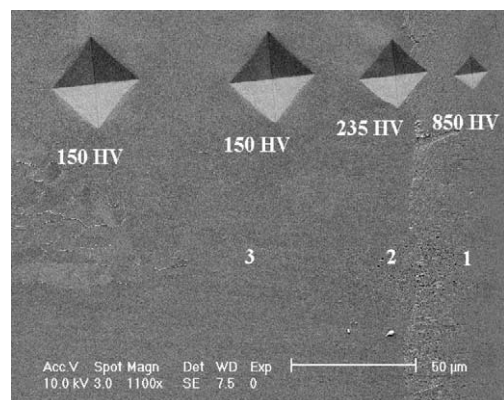


Fig. 3. SEM image of the pure iron treated at 850 °C for 10 min, showing the hardness indentation variation from the outer layer to the interior.

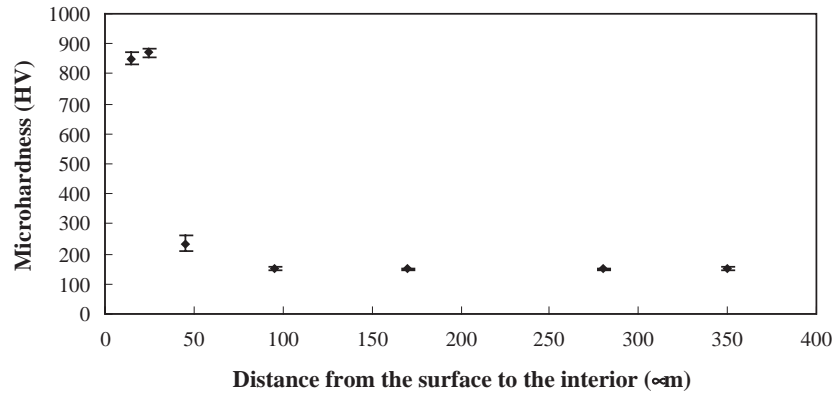


Fig. 4. Microhardness vs. distance from the surface to the interior for the pure iron treated at 850 °C for 10 min.

SEM images of the carbon-rich layer formed on the iron substrates for 5, 10, 30, and 60 min are shown in Fig. 2(a–d), respectively. Three regions appear in Fig. 2(a–d), namely: (1) a layer consisting of a dense needle-like structure; (2) a diffusion/transition zone between the layer and the substrate, presumably rich in carbon; and (3) the substrate material, which is untreated pure iron. Although it is difficult to distinguish region 2 from region 3 in Fig. 2(a–d), microhardness indentation made it possible to differentiate these two regions as shown in Fig. 3.

3.2. Hardness of the carburized layer

Fig. 3 shows the hardness indentation variation from the outer layer to the interior for the sample treated at 850 °C for 10 min. The hardness of carburized layer is 850 HV, whereas the hardness of the substrate is 150 HV. Fig. 4 also demonstrates the changes in hardness values from the

surface to the interior of the carburized pure iron. From both figures, it is clear that the hardness of carbon-rich layer formed on the surface of pure iron is much higher than that of the substrate due to the presence of hard carbon-rich content.

3.3. X-ray diffraction

Fig. 5 reveals the X-ray diffractions of the untreated pure iron, the treated iron for 5 min, and the treated iron for 10 min. It can be seen from the diffraction pattern that there is a clear difference between untreated and treated samples, although there is no big difference between the treated samples of 5 and 10 min in terms of intensity and existence of the peaks. The presence of mixture of Fe₃C, martensite, BCC iron, and FCC iron for the samples treated for 5 and 10 min was evaluated from an X-ray study of the diffraction patterns by means of a software database of JCPDS.

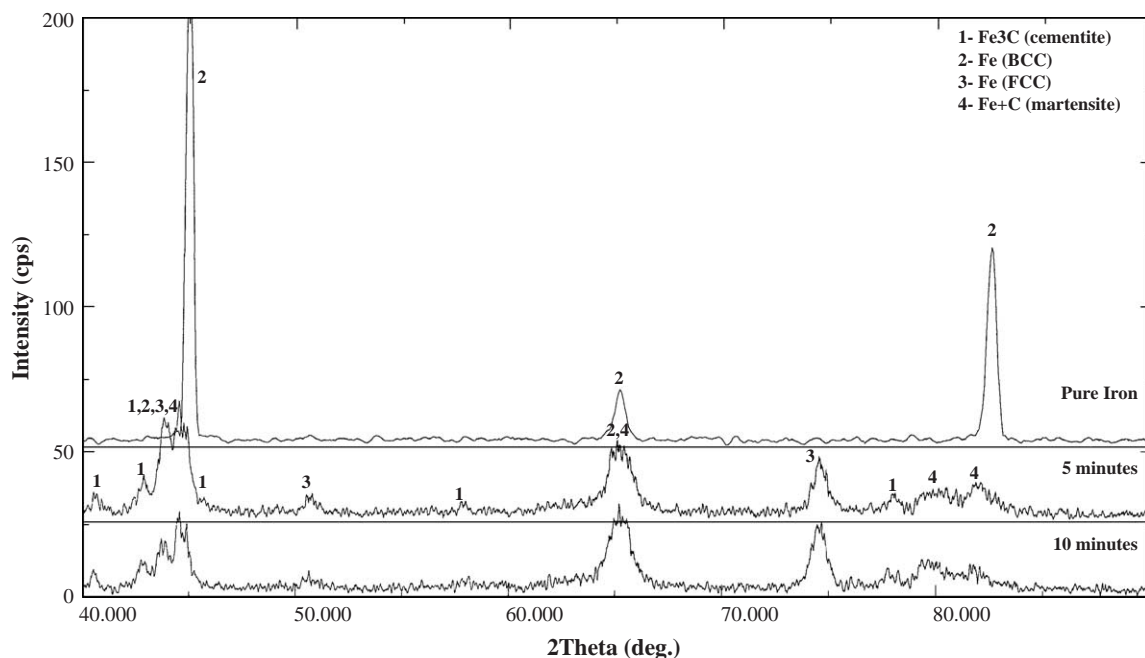


Fig. 5. X-ray diffraction patterns of three samples of pure iron, 5-min-treated sample, and 10-min-treated sample from up to down, respectively.

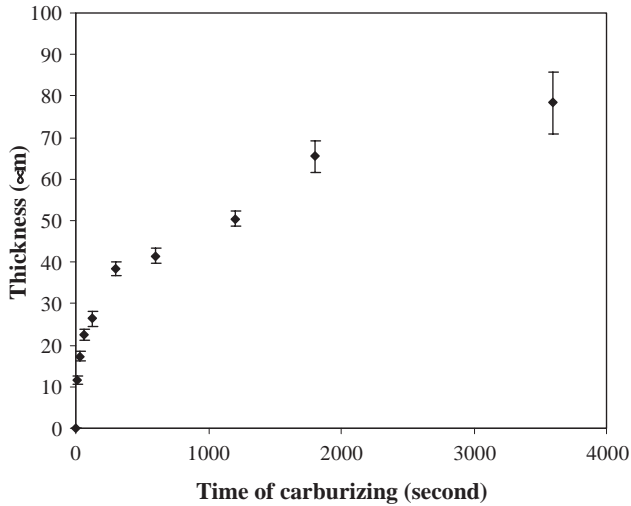


Fig. 6. Change in thickness of carburized layer with process time.

3.4. Thickness of the carburized layer

Fig. 6 indicates the depth of the carbon-rich layer as a function of process time. It can be seen from the figure

that the longer the process time, the thicker the carburized layer. It should also be noted that the maximum thickness obtained in the process was about 80 μm for the maximum process time of 1 h.

3.5. Elemental analysis of the coated pure iron

Electron dispersive spectra (EDS) study was performed to investigate whether this process was actually a pure carburizing process or not. For this, EDS study was performed on the coated layer and on the base metal. Fig. 7a and b shows EDS spectra from the coated layer and the base material. Fig. 7a confirms the presence of carbon and iron peaks. However, Fig. 7b shows no indication of carbon peak, but only iron peak from the base material. Further elemental studies were needed to confirm the only carbon diffusion into the surface. The elemental distributions from the coated layer by RF-Glow Discharge Optical Emission Spectrometry (GDOES) shown in Fig. 8 indicate only major elements carbon, iron, and some trace elements of hydrogen and nitrogen. Both EDS and RFGDOES studies verify only

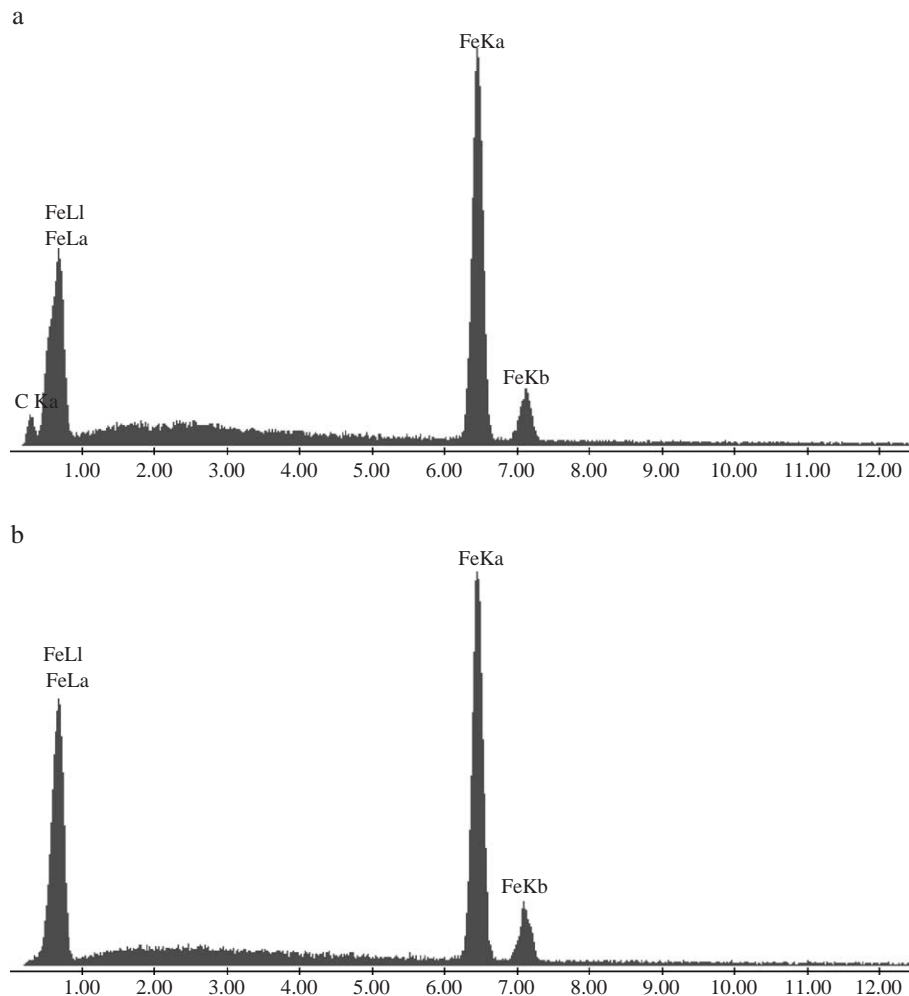


Fig. 7. (a) EDS spectra from the coated layer, showing carbon and iron peaks. (b) EDS spectra from the base metal, showing no peaks, except Fe peaks.

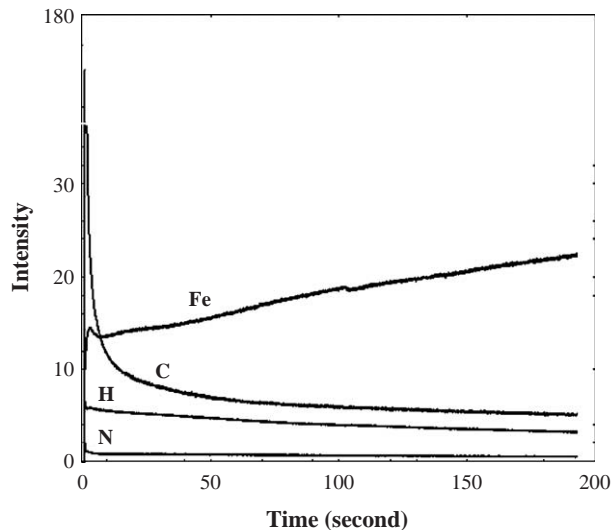


Fig. 8. The relative concentration of the elements found on the coated layer and their distribution from the coated layer to the interior.

the diffusion of carbon through the base material, not the other elements.

4. Discussion

The scanning electron microscopy (SEM) cross-sectional examinations revealed that the carburized layer formed on pure iron is nearly dense and closely contiguous to the metal base (Fig. 2a–d). Hardness measurements showed three different regions (Fig. 3). These are: a surface layer marked as (1) consisting of a mixture of Fe_3C , martensite, BCC iron, and FCC iron phase; a diffusion/transition zone marked as (2), presumably rich in carbon; and the substrate marked as (3). The presence of the phases on the surface was evaluated from qualitative X-ray study (Fig. 5).

The occurrence of BCC and FCC iron phases can be attributable to the fact that the temperature of the samples to be carburized in electrolyte was $850\text{ }^\circ\text{C}$ where two phase regions ($\alpha+\gamma$) co-exist in Fe–C phase diagram. As the temperature was not high enough to be in austenite (γ) single region, ferrite phase (α) was observed by X-ray diffraction. Another reason might be that the X-ray peak of BCC iron (substrate) under the carburized layer can be observed. FCC iron could be a retained austenite because austenite phase might be suppressed in the structure due to the fact that martensite finish temperature (M_f) can be below room temperature because of high carbon content occurring during carburization process. The formation of martensite is simple to understand because the carbon atoms are dissolved in austenite and forced to be trapped in ferrite phase, leading to martensite when the sample is quenched. It was reported [2] that if carburizing has been properly carried out, the core will still be of low carbon content (0.1–0.2% C), while the case should preferably have a carbon content of no more than 0.8% C (the eutectoid composition). If the carbon content of

the case is higher than this, then a network of primary cementite will coincide with the grain-boundary sites of the original austenite, giving rise to intercrystalline brittleness and consequent peeling of the case during service. It is assumed that the carbon content of the carburized layer is presumably more than 0.8% C based on the observation of cementite (Fe_3C) in the present study. Hardness measurements carried out by means of Vickers indentation from the surface to the interior of the specimen indicated that the hardness of carburized layer was much higher than that of the substrate (Figs. 3 and 4). This is the consequence of the presence of hard Fe_3C and martensite as qualitatively determined by X-ray diffraction (Fig. 5). The hardness values of the carburized layer, the layer just below the carburized layer and the substrate, are 850, 235, and 150 HV, respectively. The reason for the higher hardness of region 2 than region 3 is a result of a solid solution hardening between iron and carbon. It was observed that the longer the carburizing time, the greater the carburized layer thickness. It is known that the thickness of carburized layer depends strongly on the carburization time, the chemical composition of material to be carburized, process temperature, and the techniques such as gas, liquid, and pack carburizing. In this study, the chemical composition of material to be carburized, process temperature, and the applied technique were fixed, and the only variable parameter was the carburizing time. The carburized layers ranged in thickness from $12\text{ }\mu\text{m}$ to $78\text{ }\mu\text{m}$, with carburizing time as shown in Fig. 6. The increase in the thickness of carburized layer is fast at the beginning and slows down with processing time. The kinetics of the growth rate for the carburized layer is beyond the scope of this study. Moreover, the further work is in progress to evaluate the carburization kinetics of pure iron in much detail by performing the process in longer times and at different temperatures, and by taking the effect of composition on the depth of carburized layer into consideration. This will be published in another paper.

One can claim that decomposition of ammonia chloride should give active nitrogen ions, which could, competitively with carbon, diffuse into the surface. In addition, it was reported in Ref. [11] that simultaneous diffusion of carbon and nitrogen into base material occurs in the electrolyte composed of C/N-containing organic compounds. Although the electrolyte used in this study consists of C/N-forming compounds such as glycerin and ammonia chloride, both carbon and nitrogen diffusions are not the case in this study. This was proved by both EDS and RF-Glow Discharge Optical Emission Spectrometry (RFGDOES) elemental analyses shown in Figs. 7a and 8. The only diffusing element found by EDS study shown in Fig. 7a is carbon. The relative concentration profiles of carbon and other elements presented in Fig. 8 show that the major elements in the coated layer are carbon and iron, and the minor elements are hydrogen and nitrogen. The hydrogen can possibly come from the emerging hydrogen at cathode surface and its profile remains constant with sputtering time or distance.

The relative carbon concentration decreases with sputtering time or distance from the surface to the interior, whereas the iron profile increases. This result is expected and confirmed by the Vickers hardness study. The concentration of carbon should be high at the surface and decrease with distance. The intensity of nitrogen is very low compared to that of the carbon. These results confirm that this study is actually a pure carburizing process.

The undergoing mechanism responsible for the electrolytic surface carburization of pure iron in aqueous solution of the present study can be explained as follows.

In an earlier study, gas film (plasma) formation was explained by the mechanism of contact glow-discharge electrolysis [11,13]. In this mechanism, by the application of voltage, a gas film starts to form on the surface of electrode; however, increasing the applied voltage results in breakdown of the conventional electrolysis and electrode (work piece) becomes covered by very intense glow [11,13]. In the present work, after 210 V DC application to the iron substrate (cathode) and the stainless steel container (anode), the immersion process is started. As soon as the sample touches the solution, a hydrogen gas film forms rapidly around the sample. Due to the formation of the hydrogen gas film around the iron substrate, the resistance between the sample and the solution increases sharply. Then the electrical discharge, including electrons, on ion avalanche occurs and this results in heat generation around the sample [11–13].

The solution and/or tiny solution droplets containing the glycerin molecules in the vicinity of the sample contact with the hot surface of the sample in short durations of times. These solutions and/or solution droplets evaporate immediately under the reducing atmosphere of hydrogen gas film, leaving the glycerin molecules on the surface of the sample. These glycerin molecules decompose and produce free carbon atoms on the hot substrate. When the sample is hot, the localized thermoionic emission of electrons from the sample to the electrolyte may occur and this localized electron emission moves around on the sample surface where the gas film is thinner. It should be noted that ionization of the carbon under this electron emission may also be possible because the ionization potential of carbon is 11.260 eV [14]. These free and/or ionized carbon atoms are the source of carbon in the present carburization process and they diffuse into the pure iron substrate at 850 °C. Furthermore, due to present DC electric current in the carburizing cell, collision between electrons and carbon atoms/ions on the substrate may also help carbon atoms/ions to penetrate into the pure iron [15].

The carburization method studied in this paper is superior to the conventional carburizing techniques for a couple of reasons. One is that the carburized samples do not require an additional heat treatment (that is to say, that the sample can be carburized, hardened, and toughened in a single operation). It is well known that in conventional carburizing methods, heat treatment is necessary to strengthen and toughen the core and harden the case after the carburization of the components. At

the same time, prolonged heating in the austenitic range during carburizing processes results in coarse grains in whole microstructure; hence a heat-treatment program which will also refine the grains is necessary to attain the optimum properties. For components which are being packed or liquid carburized to produce deep cases, a double heat treatment is preferable to refine both core and case separately, as well as to harden the case and strengthen the core [2].

The other, the most important, reason is that the present method can be used to carburize pure iron and steel containing a much lower carbon content than the usual alloys with 0.10% C.

The studies on electrolytic surface hardening process in the literature [7–10] were performed for the surface hardening of AISI 1050 steel. In these electrolytic surface hardening processes, the steels with high enough carbon content were hardened by heating and quenching without any carburization treatment. In addition, the process was used to carburize the mild steel (0.4% C+1% Cr) or low carbon steel (SAE 1020) as well [11]. In the present process, pure iron and steels with very low carbon content can be carburized and hardened successively in a single operation. This enables producers to shorten the process time and benefit from very low carbon steels.

5. Conclusions

The following conclusions can be drawn from the present study:

- 1) The carburized layer formed on the pure iron has a smooth and dense morphology.
- 2) The microstructural studies and hardness measurements show three distinct regions: (1) a dense, smooth, and hard surface layer; (2) the transition layer, which has a higher hardness value than the base metal; and (3) base metal of pure iron.
- 3) The hardness of the carburized layer on the substrate is about 850 HV, while the hardness of the substrate is about 150 HV.
- 4) The dominant phases formed on the pure iron are found to be a mixture of Fe₃C, martensite, BCC iron, and FCC iron confirmed by XRD.
- 5) Depending on carburizing time, the depth of carburized layer formed on the surface of pure iron substrate ranges from 12 to 78 μm with some scatters.
- 6) Elemental analysis shows that carbon is the dominant element that diffuses into the pure iron, proving that the process used in this study is a carburizing process.

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