Specificity of carbon diffusion during plasma electrolytic treatment of steel

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Abstract. This work is devoted to evaluation of the diffusion coefficient of carbon using the thickness of the martensitic layer after plasma electrolytic carburising in various electrolytes followed by quenching. The effective diffusion coefficients of carbon in the structure of mild steel containing oxide and martensitic layers are determined. The maximum diffusion coefficient at a carburising temperature of 900 °C is $23.6 \times 10^{-8}$ cm$^2$/s for treatment in an acetone-based electrolyte for 1 min. The obtained values were comparable with the calculation results for the thickness of the pearlite layer after anodic plasma electrolytic carburising as well as data of measurements of the distribution of carbon concentration in the carburised layer after cathodic saturation. The influence of the oxide layer inhibiting the diffusion of carbon and the possibility of controlling its thickness by varying the concentration of ammonium chloride, which provides anodic dissolution of steel, were confirmed.

1. Introduction

A specific feature of the plasma electrolytic carburizing (PEC) is a more complex three-phase system (electrolyte solution, vapour-gas envelope (VGE), metal electrode) compared to traditional carbon saturation from a solid or gas phase [1]. Firstly, the saturation temperature depends on the heating voltage, the polarity of the workpiece, the composition of the electrolyte, its temperature and the hydrodynamic conditions in the electrolyser. Secondly, the diffusion saturation with carbon is further complicated by the inevitable chemical and electrochemical reactions, as well as by the action of electric discharges in the VGE. These PEC features determine the kinetics of carbon saturation of steels obtained by various authors.

Electric discharges in VGE during cathodic PEC create unsteady heat sources, which makes it difficult to measure the temperature directly in the carburised material, where carbon diffusion takes place. For these reasons, the effect of the PEC duration on the layer thickness is different. For example, the increasing time dependence of the thickness of the carburised layer during the treatment of pure iron in a glycerol-based electrolyte is not parabolic [2], therefore, the surface carbon concentration during saturation cannot be considered constant. However, the saturation of mild steel with carbon in a 25 wt. % solution of potassium acetate in glycerol leads to a parabolic dependence of the layer thickness on the processing time [3]. It can be assumed that a constant concentration of carbon on the surface of the steel is achieved by additional stabilization of the conditions in the VGE owing to the use of two current sources (direct and high-frequency current). A surface carbon concentration of 1.4 wt. % is determined for PEC in a solution of potassium acetate in glycerol at 950 °C and a frequency of 350 Hz [4]. The carbon potential is also measured at the PEC of low-carbon
steel (900 °C, 15 min) in an aqueous solution containing 10 wt. % sodium carbonate and 20 wt. % ethanol equal to 0.7 wt. % [5]. The temperature conditions and structure of the layers obtained in these examples reveals that carbon diffuses in austenite.

The anodic PEC occurs under almost stationary conditions without electric discharges in the VGE, which enables to measure the temperature of a workpiece or sample with acceptable accuracy. As a rule, the dependence of the thickness of the martensitic layer after PEC followed by quenching on the saturation time is parabolic [6].

The carbon potential of electrolytes at the anodic PEC is estimated using various methods. The area of the portions of cementite in the form of a grid did not exceed 2 % in the layer. In this case, the carbon potential of VGE is taken equal to 0.9 wt. %. The potential of 0.8 wt. % corresponds to the absence of a cementite network and ferrite grains. The appearance of ferrite grains occupying an area of up to 10 % of the area of perlite grains permits to estimate the carbon potential as 0.7 wt. % [7].

The simplest example of estimating the carbon diffusion coefficient is the experimental measurement of the weight a thin wire of low-carbon steel after its anodic PEC in a solution of glycerol and ammonium chloride at 180–240 V [8].

The carbon diffusion coefficient at the anodic PEC is also estimated from the measurements of the average carbon concentration at a given depth using emission spectral analysis [9]. A well-known solution of the diffusion equation for a semi-infinite body modified by the introduction of an average volume concentration $\bar{C}$:

$$C = C_0 + \left( \frac{C - C_0}{F(D)} \right) \text{erfc} \left( \frac{x}{2\sqrt{Dt}} \right), \quad (1)$$

where $C$ – is the carbon concentration at depth $x$, $C_0$ – is the initial carbon concentration, $D$ – is the carbon diffusion coefficient in steel, $t$ – is time, $\text{erfc}(x)$ – is an additional error function.

The carbon content in the pearlite layer being 0.76 wt. % is chosen to determine the diffusion coefficient [10]. The depth of the layer is determined optically. The diffusion coefficient of carbon is $1.29 \cdot 10^{-8}$ cm$^2$/s at 900 °C.

Determining the thickness of a pearlite layer requires an additional operation of tempering or cooling the sample in air after PEC. In the latter case, incomplete hardening of carburised steel is not excluded. The aim of this article is to verify an alternative version for estimating the diffusion coefficient of carbon using the thickness of the martensitic layer, which is easily visually determined after etching of the sample or by the distribution of microhardness in the layer. In this case, the carbon concentration at the boundary of the martensitic layer is taken to be 0.26 wt. % [10]. The carbon diffusion coefficient is found by numerically solving equation (1) using known estimates of the carbon potential of VGE formed in electrolytes of various compositions.

2. Materials and equipment

Cylindrical samples of low-carbon steel (0.1 wt. % C) with a height of 20 mm and a diameter of 10 mm were subjected to anodic PEC. All samples were cleaned with sandpaper to a surface roughness of Ra 1.01 μm and washed with ultrasound in acetone before processing. The PEC was carried out in a cylindrical axisymmetric electrolyser with a longitudinal flow around the samples with electrolyte supplied through a nozzle located in the bottom of the chamber.

After applying voltage, the samples were immersed in the electrolyte to a depth equal to the height of the samples. After PEC, the samples were quenched in the electrolyte from the saturation temperature. The heating temperature of the samples varied from 800 to 1000 °C, the processing time was 1, 3 and 7 minutes. An aqueous solution of ammonium chloride and one of the carbon-containing components: acetone, ethylene glycol, glycerol, sucrose, ethyl and isopropyl alcohol were used as a working electrolyte. The concentration of carbon-containing components of the electrolyte was 10 wt. %, the concentration of ammonium chloride was also 10 wt. %.
The structure of the surface layer of the samples was studied using an EC METAM RV-21 optical microscope after polishing and etching (4 wt. % solution of nitric acid in ethanol) for 5–10 s.

3. Results and discussion
First of all, we evaluate the carbon potential of glycerol-based electrolytes and the diffusion coefficient of carbon over the thickness of the martensitic layer using the previously published data [9] and compare them with the data obtained for the pearlite layer (table 1).

**Table 1.** Conditions and results of evaluating the diffusion coefficient of carbon and the carbon potential of glycerol electrolyte during anodic PEC [12]. Nomenclature: $C_{gl}$ is glycerol concentration, $C_{ch}$ is ammonium chloride concentration, $T$ is PEC temperature, $t$ is PEC duration, $\delta_p$ is pearlite layer thickness, $\delta_m$ is martensitic layer thickness, $C_V$ is volumetric carbon concentration in a layer of 75 $\mu$m thick, $D_1$ is carbon diffusion coefficient (pearlite calculation), $C_{S1}$ is surface carbon concentration (pearlite calculation), $D_2$ is carbon diffusion coefficient (martensite calculation), $C_{S2}$ is surface carbon concentration (martensite calculation).

| $C_{gl}$ (wt.%) | $C_{ch}$ (wt.%) | $T$ ($^\circ$C) | $t$ (min) | $\delta_p$ (µm) | $C_V$ (wt.%) | $D_1 \cdot 10^8$ (cm²/s) | $C_{S1}$ (wt.%) | $\delta_m$ (µm) | $C_{S2}$ (wt.%) | $D_2 \cdot 10^8$ (cm²/s) |
|----------------|----------------|----------------|-----------|----------------|-------------|--------------------------|----------------|----------------|----------------|--------------------------|
| 5              | 10             | 900            | 5         | 0.48           | 3.5±0.4     | 0.93                     | 66             | 0.85           | 4.7±0.5       | 8.8±0.8                   |
| 10             | 10             | 1000           | 5         | 0.56           | 7.8±0.8     | 0.86                     | 90             | 0.84           | 8.8±0.8       | 8.8±0.8                   |
| 10             | 10             | 900            | 10        | 0.69           | 6.8±1.7     | 0.95                     | 102            | 1.03           | 4.6±0.3       | 4.6±0.3                   |

Data of table 1 show that the obtained values of the diffusion coefficient are close, while the carbon potential practically coincides for a heating temperature of 1000 $^\circ$C. Hence, the minimum concentration in the martensitic layer can be used as a characteristic carbon concentration.

Table 2 contains the experimental data on the anodic PEC of low-carbon steel in electrolytes of various compositions. The carbon potentials of electrolytes are determined by measuring the surface concentration of carbon using spectroscopy of proton nuclear backscattering [11].

Figure 1 shows the dependence of the square of the thickness of the martensitic layer on the processing time for electrolytes based on glycerol and sucrose. The obtained dependences correspond to a constant concentration of carbon on the surface of the sample.

This fact indicates a rather rapid adsorption of carbon on the treated surface, which is one of the advantages of PEC. The influence of the temperature of the PEC on the diffusion coefficient of carbon is quite standard for electrolytes containing glycerol or ethylene glycol (figure 2). The exponential dependence for other solutions is less pronounced, which may be associated with the growth of the oxide layer and its uncontrolled destruction.

![Figure 1](image1.png) **Figure 1.** The dependence of the square of the thickness of the martensitic layer on the processing time at 1000 $^\circ$C in glycerol and sucrose electrolytes.

![Figure 2](image2.png) **Figure 2.** The dependence of the coefficient of carbon diffusion on the temperature of the PEC in glycerol or ethylene glycol electrolytes.
Table 2. Experimental data and results of evaluating the coefficient of carbon diffusion in various electrolytes with carbon-containing components at the anodic PEC. Nomenclature: \( T \) is the saturation temperature, \( t \) is the duration, \( U \) is the voltage, \( I \) is the current, \( \delta_m \) is the thickness of the martensitic layer, \( D \) is the diffusion coefficient of carbon.

| Component (carbon potential) | \( T \) (°C) | \( t \) (min) | \( \delta_m \) (µm) | \( D \cdot 10^8 \) (cm²/s) |
|-----------------------------|---------------|----------------|-----------------|------------------|
| Acetone (0.9 %)             | 800           | 3              | 65              | 1.23             |
|                            | 850           | 3              | 65              | 0.93             |
|                            | 900           | 3              | 65              | 1.67             |
| Glycerol (0.8 %)            | 800           | 1              | 16              | 3.17             |
|                            | 850           | 3              | 36              | 3.23             |
|                            | 900           | 3              | 54              | 5.35             |
|                            | 950           | 3              | 72              | 9.51             |
|                            | 1000          | 3              | 84              | 12.90            |
|                            | 1000          | 3              | 84              | 13.70            |
| Ethylene glycol (0.6 %)     | 800           | 1              | 6               | 0.28             |
|                            | 850           | 3              | 18              | 1.13             |
|                            | 900           | 3              | 30              | 2.35             |
| Isopropanol (0.8 %)         | 800           | 3              | 33              | 1.75             |
|                            | 850           | 3              | 97              | 6.48             |
|                            | 900           | 3              | 102             | 16.71            |
|                            | 850           | 1              | 1                | 2.54             |
|                            | 900           | 3              | 102             | 3.23             |
|                            | 950           | 3              | 102             | 3.23             |
|                            | 1000          | 3              | 102             | 3.23             |
| Sucrose (0.7 %)             | 800           | 3              | 33              | 1.75             |
|                            | 850           | 3              | 97              | 6.48             |
|                            | 900           | 3              | 102             | 16.71            |
|                            | 850           | 1              | 1                | 2.54             |
|                            | 900           | 3              | 102             | 3.23             |
|                            | 950           | 3              | 102             | 3.23             |
|                            | 1000          | 3              | 102             | 3.23             |
| Ethanol (0.6 %)             | 800           | 3              | 33              | 1.75             |
|                            | 850           | 3              | 97              | 6.48             |
|                            | 900           | 3              | 102             | 16.71            |
|                            | 850           | 1              | 1                | 2.54             |
|                            | 900           | 3              | 102             | 3.23             |
|                            | 950           | 3              | 102             | 3.23             |
|                            | 1000          | 3              | 102             | 3.23             |

The various carbon potentials of the studied electrolytes are related to the boiling point of carbon-containing components. The boiling point of these components affects the intensity of its evaporation into the VGE. The lower boiling point of acetone contributes to its higher concentration in the saturating medium. In addition, a lower density of acetone determines a higher mobility of the molecules in the aqueous solution, which also increases the rate of its evaporation into the VGE.

The diffusion coefficients of carbon substantially depend on the composition of the electrolyte (table 3). This fact is explained by the different composition of the carburised layer. The highest values of the diffusion coefficient of carbon are reached with a minimum content of oxides in the carburised layer, inhibiting the transfer of carbon atoms. The diffusion coefficient of carbon increases by about 3 times due to an increase in the concentration of ammonium chloride, which provides more intensive anodic dissolution reducing the thickness of the oxide layer. The growth of the oxide layer with increasing temperature or saturation time, as well as with a decrease in the concentration of
ammonium chloride are detected during the processing of low-carbon steel in a solution containing glycerol, ammonium chloride, and ammonium nitrate [12].

Table 3. The effective coefficient of carbon diffusion $D$ at the anodic PEC in various electrolytes. The PEC temperature is 900 °C, the duration is 5 min.

| Electrolyte                  | 10% glycerol and 10% NH$_4$Cl | 5% glycerol and 10% NH$_4$Cl | 10% glycerol and 15% NH$_4$Cl | 10% acetone and 10% NH$_4$Cl |
|-----------------------------|-------------------------------|-------------------------------|-------------------------------|-------------------------------|
| $D \cdot 10^8$ (cm$^2$/s)   | 0.78±0.12                     | 3.5±0.4                       | 12.9±1.6                      | 12.5±1.7                      |

Another confirmation of the inhibitory role of the oxide layer is a decrease in the carbon diffusion coefficient as the PEC duration increases (table 2). This trend is observed for the electrolytes containing acetone, ethylene glycol, ethanol and isopropanol, when the temperature of the PEC is high enough for a significant growth of the oxide layer.

4. Conclusions
The thickness of the martensitic layer can be used to estimate the diffusion coefficient of carbon under conditions of plasma electrolytic carburising with subsequent quenching in the same electrolyte.

The estimates of the diffusion coefficients of carbon in steel during anodic plasma electrolytic carburising in various electrolytes are obtained. The highest diffusion coefficient of carbon reaches 23.6$\cdot 10^{-8}$ cm$^2$/s (900 °C, 1 min) for an acetone-based electrolyte with minimal oxidizing ability.

The possibility of accelerating carbon diffusion by intensifying the anodic dissolution of the outer oxide layer inhibiting carbon diffusion is shown.

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