Vacuum Carburizing of Low Carbon Steel with Methane

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On low carbon steel specimens vacuum carburized at temperatures in the range from 1193 to 1313 K in a methane atmosphere at pressures ranging from 13 to 80 kPa, carbon content profiles within the specimens were determined from a succession of grindings and carbon analyses with a vacuum type emission spectrometer. The total amount of carbon which entered each specimen through the surface during a carburizing period was graphically calculated from the profile, and the rate of carburizing was evaluated from the amount of carbon. It was found that the rate of vacuum carburizing with methane had the temperature dependence several times as strong as that of gas carburizing. A mathematical model for calculation of such carbon content profiles is presented. The model in which the variation of carbon diffusion coefficient in steel with carbon content was taken into consideration predicted accurately the surface carbon content and case depth of vacuum carburized steel.

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I. Introduction

Some reports(1)-(3) have been published on introduction and technical explanation of vacuum carburizing process or on comparison of vacuum carburizing with gas carburizing. Some studies(4)(5) concentrating on microstructures and mechanical properties of vacuum carburized steels have been done. Papers on effects of process variables on the surface carbon content and case depth, however, have apparently not been presented for vacuum carburizing, though many varieties of studies(6)-(11) on those have been done for gas carburizing up to date.

The quality of carburized part is usually checked with microhardness profiles in commercial practice, but it, in principle, should be dependent on a carbon content profile. It is, therefore, essential for accurate and repeatable quality control of vacuum carburized process to establish theoretical relationships of process variables with carbon content profiles. It is the purpose of this study to clarify effects of temperature, time and methane pressure on the surface carbon content and the uptake amount of carbon by steel, and to construct a mathematical model which enables one to calculate carbon content profiles in vacuum carburized and/or diffused steels.

II. Experimental Procedure

Carburizing specimens were prepared by lathing and grinding low carbon steel bars having a chemical composition of C: 0.17, Si: 0.19, Mn: 0.53, P: 0.008 and S: 0.021 mass% into the geometry and dimension as shown in Fig. 1. The methane gas used contained impurities such as CO₂, N₂ and O₂ under 1 vol%.
The experiments were carried out in a longitudinal furnace, equipped with a 35 mm diameter quartz tube and an oil container for quenching. The experimental set-up is shown in Fig. 2. After the specimen was brought to a given temperature between 1193 and 1313 K and then maintained at the temperature for about 600 s under a pressure below 0.13 Pa, the methane gas from which water vapor and hydrogen sulfide were removed by making it pass through potassium hydroxide and silica gel was introduced at the top of the quartz tube. During the carburizing period, the methane in the tube was kept at a given pressure between 13 and 80 kPa and at a constant flow rate of 3.4 cm$^3$/s by a light receiver attached to a Bennet type vacuum gauge and a solenoid valve connected with it. Some preliminary experiments showed that the rate of carburizing did not depend upon the flow rate of methane over the range from 2.1 to 7.6 cm$^3$/s. After the carburization, the reaction tube was back-filled with a purified Ar gas to atmospheric pressure, and immediately the specimen was oil quenched.

Successive removal of a thin layer in the range from 40 to 150 μm from each carburized specimen was made with a horizontal type surface grinding machine. After each removal, a depth determination from the original surface was made by measuring the thickness with a micrometer, and a carbon analysis was performed on the surface by a vacuum type emission spectrometer (Vacuum Quantorecorder GVM-1000). Figure 3 shows the surface roughness of a carburized specimen after carbon analysis by a vacuum type emission spectrometer.

![Fig. 3 Surface roughness of a carburized specimen after carbon analysis by a vacuum type emission spectrometer.](image)

V. Experimental Results

The change in carbon content as a function of distance below the surface is shown in Fig. 4, as an example, for the specimen carburized at 1273 K for 3600 s in a methane atmosphere at 26.7 kPa. The surface carbon content was determined by extrapolating each series of measured points to the surface. Figure 5 shows variations of such surface carbon content with square root of time for the specimens carburized at 1273 K. As clear from Fig. 5, the surface carbon content rises approximately linearly with $\sqrt{t}$ until about 12.1 ks at 26.7 kPa, and until about 2.5 ks at 53.3 kPa. For longer times than $t_{\text{sat}}$ the surface carbon content remains constant as in Fig. 5, where $t_{\text{sat}}$ is the time at which the surface carbon concentration reaches $c_{\text{sat}}$, i.e., the carbon concentration at which the steel is saturated. The X-ray diffraction results obtained showed no deposition of graphite on the specimens for shorter times than $t_{\text{sat}}$, but did its deposition for the longer times as in Fig. 6.

We denote $M$ by the total amount of carbon, expressed as the number of moles per unit
area, which has entered the steel in time $t$. For the shorter times $M$, which was graphically evaluated from the carbon content profile obtained, varies as a linear function of $t$ as shown in Fig. 7, i.e.

$$M = Ft, \quad t < t_{\text{sat}},$$  \hfill (1)

where $F$ is the rate of carburizing. The condition expressed by eq. (1) can be identified with

$$-D \frac{\partial c}{\partial x} = F, \quad x = 0, \quad t < t_{\text{sat}},$$  \hfill (2)

where $D$ is the diffusion coefficient of carbon in the $\gamma$-Fe, and $c$ the carbon concentration in the number of moles per unit volume.
A typical cross-sectional microstructure is shown in Fig. 8 for a specimen carburized at 1273 K for 3600 s in a methane atmosphere at 26.7 kPa and then oil quenched in an Ar atmosphere. The structure was identified with the one consisting of martensite, fine pearlite and retained austenite by X-ray diffraction analysis. The surface carbon content of the specimen was 0.90 mass% according to the measured carbon content-distance curve.

For longer times than \( t_{\text{sat}} \), the experimental results showed a gradual increase in \( M \) with \( t \). This implies that the graphite layer deposited on the surface substantially throws no appreciable hindrance, if any, in transfer of carbon into steel. It perhaps may be feasible that the graphite layer has narrow pores through which carbon transfers from the gas phase into steel. However, it seems to be more reasonable that transfer of carbon occurs from the graphite layer itself into steel, on referring to experimental results by Mitani et al.\(^{12}\) They studied on the sintering of Fe–C binary mixed powder compacts in a H\(_2\) atmosphere and under a high vacuum, and concluded that the carburization was done mainly by carbon transfer through the contacting surface of graphite and iron powder rather than through the medium CH\(_4\) or CO gas generated by the interreaction of graphite and the residual or absorbed oxygen. From this, and from the constancy of the surface carbon content as shown in Fig. 5, it follows that diffusion of carbon in steel is the rate limiting step for the longer times. Then, the boundary condition can be written as

\[
c_t = c_{\text{sat}}, \quad t > t_{\text{sat}},
\]

where \( c_t \) is the carbon concentration at the surface of carburized steel.

The dependence of \( F \) on methane pressure at 1273 K is shown in Fig. 9. Below the critical pressure, about 10 kPa, the methane gas has no carburizing ability, but above that \( F \) increases in proportion to a difference between the applied and the critical pressure, as clear from Fig. 9. In Fig. 10 the temperature dependences of \( F \) are shown at methane pressures of 26.7 and 53.3 kPa. A discrepancy in \( F \) between the two applied pressures increases rapidly with temperature, as seen in Fig. 10. Their activation energies amount to 309 and 380 kJ, respectively. Kaczala et al.\(^{13}\) gravimetrically measured the rate constants of carburizing for the gas carburizing atmosphere consisting of an endothermic carrier gas enriched with C\(_3\)H\(_8\) from 0.4 to 1.4\%, and from their temperature dependences they estimated the activation energies to be in the range from 73.7
to 87.5 kJ. Here the boundary condition for the process of gas carburizing may be expressed by

\[ \frac{\partial c}{\partial t} = D_{sat} \frac{\partial}{\partial x} \left\{ \theta(c) \frac{\partial c}{\partial x} \right\} = D_{sat} \left\{ \frac{\partial \theta(c)}{\partial x} \frac{\partial c}{\partial x} + \theta(c) \frac{\partial^2 c}{\partial x^2} \right\}, \quad (6) \]

where \( \theta(c) = \frac{D}{D_{sat}} \), and \( D \) and \( D_{sat} \) are the carbon diffusivities at a given carbon content and at the content \( c = c_{sat} \), respectively. Writing \( X = x/l, T = D_{sat} t/l^2 \) and \( C = (c - c_b)/(C_{sat} - c_b) \), where \( l \) is the half thickness of a plane sheet and \( c_b \) is the base carbon concentration, gives

\[ \frac{\partial C}{\partial T} = \frac{\partial \theta(c)}{\partial X} \frac{\partial C}{\partial X} + \theta(c) \frac{\partial^2 C}{\partial X^2}, \quad (7) \]

as the non-dimensional form of eq. (6).

We divide the range in the space into equal intervals \( \delta X \) and the time into equal intervals \( \delta T \). Then the \( X-T \) region is covered by a grid of rectangles of sides \( \delta X, \delta T \). We designate the value of carbon concentration at the grid point \( (i\delta X, j\delta T) \) as \( C_{i,j} \), where \( i \) and \( j \) are integers. With an explicit method\(^{(14)}\), eq. (7) can be written as the following finite difference equation, i.e.

\[ C_{i,j+1} - C_{i,j} = \gamma \left[ (\theta_{i+1,j} - \theta_{i-1,j})(C_{i+1,j} - C_{i-1,j})/4 + \theta_{i,j}(C_{i+1,j} - 2C_{i,j} + C_{i-1,j}) \right], \quad (8) \]

where \( \gamma = \delta T/(\delta X)^2 \). Although not a few studies\(^{(15)-(19)}\) on the carbon diffusivity in austenite for the Fe–C binary system have been done over the past years, the one by Wells et al.\(^{(16)}\) appears most reliable of them over a wide range of both carbon content and temperature. The activation energy \( Q \) and the frequency factor \( D_0 \) given by Wells et al., by use of the least squares method, can be approximated by

\[ Q(kJ/mol) = 154.2 - 4.29N_c - 0.236N_c^2 \quad (9) \]

and

\[ D_0(m^2/s) = (47.1 - 11.69N_c + 0.838N_c^2) \times 10^{-6}, \quad (10) \]

where \( N_c \) is the carbon content in at\%. Here \( D \) can be written as

![Fig. 10 Temperature dependence of the rate of carburizing.](image-url)
where $T$ is the temperature in K and $R$ the gas constant. Figure 11 shows the variation of carbon diffusivity with carbon content, calculated from eqs. (9), (10) and (11). The boundary conditions, eqs. (2), (3) and (5), can be converted into the corresponding finite difference equations, i.e.,

$$D = D_0 \exp \left(-\frac{Q}{RT}\right),$$  
$$\frac{C_{i,j}-C_{j-1,j}}{2\delta x} = F', \quad i=0, 1, \ldots, n$$

and

$$C_{i,j} = C_{i-1,j},$$

where $F' = Ft / \{D_{sat}(c_{sat} - c_b)\}$. Eliminating $C_{i,j}$ between eqs. (8) for $i=0$ and (12), and between eqs. (8) for $i=0$ and (14) gives the surface carbon concentrations, respectively, i.e.,

$$C_{i,j+1} = C_{i,j} + \gamma \{F' \delta x (3 - \theta_{1,j}/\theta_{0,j}) + 2\theta_{0,j}(C_{1,j}-C_{0,j})\} \quad (15)$$

and

$$C_{0,j+1} = C_{0,j} + 2\gamma \theta_{0,j}(C_{1,j}-C_{0,j}). \quad (16)$$

Here, in order to eliminate the fictitious diffusivity ratio $\theta_{i,j}$ from eq. (8) for $i=0$, a relationship of the form

$$\theta_{i,j} - \theta_{i,j} = 2(\theta_{0,j} - \theta_{1,j})$$

was assumed.

The calculation of a carbon profile proceeds in the following manner. An initial profile is given as $C_{i,0} = 0$ for $i = 0, 1, \ldots, n$ for the carburizing step, or given as $C_{i,0} = f(i)$ for the diffusion step, where $f(i)$ is the carbon concentration given as a function of distance at the end of the carburizing step. The value for a new surface carbon concentration can be calculated from eqs. (15), (13) and (16). Then, the values for carbon concentration term below the surface can be calculated from eq. (8) in terms of the old concentrations and also the corresponding diffusivity ratios. After each profile generation, the values for carbon concentration and its corresponding diffusivity ratio can be used for the next time increment.

In the finite difference technique, stability requires that $\gamma < 1/2^{(14)}$. The accuracy of this finite difference technique for the boundary condition, eq. (2), was established by comparison of the numerical results with the analytical solution for the case $D = \text{const.}$, and by comparison of $M$ with the product of $F$ and $t$ for the case $D = \theta(c)$, which represented the carbon diffusivity to be a function of carbon content. That is, the relative error between $M$ and $Ft$ for $t < t_{sat}$ remained less than 0.4%, where $M$ showed the value obtained from a numerical integration along the calculated profile and $F$ the value of input data as the rate of carburizing.

V. Numerical Results and Discussion

Carbon content profiles for $t < t_{sat}$ calculated according to the procedure given in section IV are presented in Fig. 12 together with experimentally determined ones, where the experimentally obtained $F$ value of $1.27 \times 10^{-3}$ mol/m²·s and composition dependent diffusivity were used for the numerical calculation. The profiles calculated for $t = 900$ and 2025 s show
a little higher carbon contents at layers near the surface than the experimental ones, respectively, as shown in Fig. 12. In each case for \( t < t_{\text{sat}} \) the above difference between the calculated and measured profiles, however, was much smaller as a whole than the one between the calculated for \( D = \text{const.} \) and the measured profile. Profiles for \( t > t_{\text{sat}} \) calculated by use of the experimentally determined \( c_{\text{sat}} \) value of 1.48 mass% are shown in Fig. 13. It is clear from the figure that the profile calculated for \( D = g(c) \) agrees well with the experimentally determined one, but none of profiles for \( D = \text{const.} \) fit the experimental one.

Calculated and measured profiles for a typical two-step process of carburizing and diffusion are shown in Fig. 14. The profile calculated for \( D = g(c) \) is much the same as the measured one. On the other hand, any profile for \( D = \text{const.} \) shows lower carbon contents at layers close to the surface, where carbon contents decrease with increasing diffusivity, and all the profiles except the case of \( D(0.6 \text{ mass%}) \) spread out more broadly in the range \( c < 0.5 \text{ mass%} \). In the first step of vacuum carburizing, carburizing is carried out at saturation, and the process temperatures which generally range from 1253 to 1323 K are much higher than those for gas carburizing. As is clear from Fig. 11, the diffusivity increases rapidly with carbon content, and also this tendency becomes more remarkable as temperature rises. Then, the disagreement between each calculated profile for \( D = \text{const.} \) and the measured one can be attributed to the strong dependence of carbon diffusivity on carbon
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content. Therefore, for simulating carbon content profiles in vacuum carburized steel, the variation of carbon diffusivity with carbon content must be taken into consideration.

A relationship between square root of carburizing time and effective case depth to 0.53 mass% at 1273 K are shown in Fig. 15. The case depths were calculated from an assumed carburizing rate of infinity and from the carburizing rates of \(1.27 \times 10^{-3}\) and \(0.482 \times 10^{-3}\) mol/m²·s which were experimentally obtained at methane pressures of 53.3 and 26.6 kPa, respectively. For the rate of carburizing having an infinite value the surface carbon content remains constant and is equal to the solubility limit regardless of carburizing time, and so the case depth obeys the parabolic law. That is, the total carburizing reaction rate is controlled by diffusion only. On the other hand, it is obvious from Fig. 15 that for such a low carburizing rate as a value of \(0.482 \times 10^{-3}\) mol/m²·s the depths seriously deviate from those rate-controlled by diffusion only. This implies that the surface reaction also must not be ignored for numerically calculating carbon content profiles in steel vacuum carburized with methane gas, especially under low pressures.

VI. Conclusion

Experiments on vacuum carburizing in a methane atmosphere at pressures of 13 to 80 kPa at temperatures in the range from 1193 to 1313 K have shown the following:

1. The total amount of carbon which has entered steel increases linearly with carburizing time until the surface carbon content reaches the solubility limit in \(\gamma\)-Fe at the temperature.

2. The graphite layer deposited on the surface, after saturation with carbon, has no substantial effect upon the rate of mass transfer of carbon into steel.

3. The rate of carburizing, \(F\), increases with temperature according to the Arrhenius law. The activation energies are about 3.5 to 5 times as large as those for gas carburizing.

4. The variation of \(F\) with methane pressure, \(P\), obeys to a formula, \(F = aP - b\), where \(a\) and \(b\) are constants with positive values.

A mathematical model has been developed for predicting carbon content profiles in vacuum carburized carbon steel. The results calculated under both conditions of \(D = \text{const.}\) and \(D = g(c)\) were compared with the experimental data. It is found that the variation of carbon diffusivity with carbon content strongly influences carbon profiles calculated in shape. The profiles calculated for \(D = g(c)\) agree with the measured ones with satisfactory accuracy.

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