An Empirical Model for Carbon Diffusion in Austenite Incorporating Alloying Element Effects

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The diffusion of carbon in austenite is important to the design and implementation of many steel heat-treating processes. The present study proposes a simple and computationally efficient equation for the diffusion of carbon in austenite for iron-carbon alloys, as well as for steels alloyed with a variety of elements. The proposed empirical model provides a pragmatic engineering approach to this important diffusion process. The model is shown to better match the carbon diffusion profiles of several carburized steel alloys, as compared to other equations that have been reported in the literature. These other equations were primarily obtained from experiments on iron-carbon alloys, and it is not surprising that they are less accurate when compared to the proposed equation that takes the full range of alloy compositions into account.

KEY WORDS: carbon diffusion; alloy effects on diffusion in austenite; empirical model; experimental data; steels.

1. Introduction

Accurate descriptions of carbon diffusion in austenite and ferrite are required in many types of steel engineering analyses. For example, strain aging and dynamic strain aging at low temperatures are controlled in part by carbon diffusion in ferrite, and models that predict aging times rely on expressions for carbon (and nitrogen) diffusion.1,2) At higher temperatures, carbon diffusion governs phase transformation kinetics during heating and cooling or during isothermal holding processes, and in several analyses, an accurate expression for carbon diffusivity in austenite is critical. As one example, carburizing models3,4) for low alloy steels require a carbon diffusivity expression that incorporates a complete assessment of the effects of alloy additions on carbon diffusion in austenite.

In this paper, existing carbon diffusion expressions in austenite are reviewed. The paper also develops a new empirical equation for carbon diffusion in austenite. This practical equation is designed to include the simultaneous effects of multiple alloy additions, as well as temperature. The new equation is also compared to previous expressions and empirical diffusion data. The applicability of the newly developed expression is illustrated through a diffusion analysis that predicts carbon profiles in several carburized steel alloys.

2. Equation Formulation and Analysis

The development of the new equation is based upon the standard form for its temperature dependence of carbon diffusion in austenite. The compositional effects are incorporated by empirically fitting experimental data for Fe–C alloys, Fe–M–C alloys (where M is a substitutional element), and plain carbon and low alloy steels.

2.1. Equation for Fe–C Alloys

Carbon diffusivity, $D$, in austenite is generally described by an Arrhenius equation of the form

$$D = D_0 \exp \left( -\frac{Q}{RT} \right)$$

(1)

where $D_0$ is the diffusivity coefficient, $Q$ is the activation energy of carbon diffusion in austenite, $R$ is the gas constant, and $T$ is absolute temperature. Values of $D_0$ and $Q$ can be determined from carbon diffusivity measurements at different temperatures. In general, the values will depend on alloy content and temperature, and may potentially depend on other parameters, including any applied stress fields, magnetic fields, or electrical fields.

Carbon diffusivity equations in austenite have been developed by multiple investigators.3–24) Table 1 summarizes several equations that were obtained by fitting functions to experimental data. Equations (2) to (7) in Table 1 assume $D_0$ and $Q$ are independent of carbon content, while Eqs. (8) to (12) in Table 1 incorporate various dependencies on carbon content and temperature. However, experimental data from Blanter (as cited in Krishtal3)), Krishtal,3) and Goldstein and Moren19) show that alloying elements can also affect carbon diffusivity. In these studies, the authors did not provide...
equations to account for the effects of alloy additions. In contrast, others have attempted to incorporate alloy additions in carbon diffusivity expressions. For example, Babu and Bhadeshia\(^\text{20}\)) demonstrated the effect of individual substitutional elements on the activity of carbon by using the Siller and McLellan equation (as cited in Babu and Bhadeshia\(^\text{20}\)). Also, Rowan and Sisson\(^\text{4}\)) described the effect of alloying elements using Thermo-Calc equilibrium calculations and experiments.

Carbon diffusivity has been experimentally shown\(^\text{5,9,11,13,14}\) to increase with an increase in carbon concentration and to increase with an increase in temperature. In the present study, the experimental carbon diffusivity data were selected to compare the equations provided in Table 1.

| Eq. No. | Equation | Ref |
|---------|----------|-----|
| (2) | \(D(T) = 0.49 \cdot \exp \left( \frac{-36000}{R \cdot T} \right)\) | 3 |
| (3) | \(D(T) = 0.668 \cdot \exp \left( \frac{37460}{R \cdot T} \right)\) | 5 |
| (4) | \(D(T) = 0.4718 \cdot \exp \left( \frac{-180590}{R \cdot T} \right)\) (by liquid carburization) | 6 |
| (5) | \(D(T) = 0.0052 \cdot \exp \left( \frac{-127950}{R \cdot T} \right)\) (by solid carburization) | 6 |
| (6) | \(D(T) = 0.0077 \cdot \exp \left( \frac{-107400}{R \cdot T} \right)\) | 7 |
| (7) | \(D(T) = 0.02 \cdot \exp \left( \frac{-112000}{R \cdot T} \right)\) | 8 |
| (8) | \(D(T,C) = (0.07 + 0.06C) \cdot \exp \left( \frac{-32000}{R \cdot T} \right)\) | 3 |
| (9) | \(D(T,C) = (0.04 + 0.08C) \cdot \exp \left( \frac{-31350}{R \cdot T} \right)\) | 3 |
| (10) | \(D(T,C) = \left(0.47263 - 0.55169C + 0.22848C^2 - 0.02965C^3\right) \cdot \exp \left( \frac{153593 - 15370C - 10727C^2 + 2432.9C^3}{R \cdot T} \right)\) | 9 |
| (11) | \(D(T,C) = 0.5 \exp(-30x_c) \cdot \exp \left( \frac{-38300 - 1.9 \times 10^3 x_c + 5.5 \times 10^3 x_c^2}{R \cdot T} \right)\) | 10 |
| (12) | \(D(T,C) = 0.47 \exp(-1.6C) \cdot \exp \left( \frac{-37000 - 6600C}{R \cdot T} \right)\) | 11 |

where \(D\) is the diffusivity of carbon in cm\(^2\)/s, \(C\) is the carbon content in mass percent, \(x_c\) is the mole fraction of carbon, \(R\) is the gas constant as 1.986 cal/mol/K, \(R \cdot J\) is the gas constant in 8.314 J/mol/K, and \(T\) is the temperature in Kelvin.

These studies were from Fe–C alloys. To assist in an assessment of the degree of fit between the experimental data and the equations, an evaluation factor (EF) was used for a quantitative comparison. The calculation of EF is given by

\[
EF = \frac{1}{N} \sum_{i=1}^{N} \left( \frac{D_{exp} - D_{cal}}{D_{exp}} \right) \quad (13)
\]

where \(N\) is the number of data points, \(D_{exp}\) is the measured diffusivity of carbon experimentally, and \(D_{cal}\) is the carbon diffusivity calculated by the individual equation. The total number of experimental Fe–C alloy data points \(N\) used here from the references cited in Table 2 is 179. Interpretation of the degree of fit between predicted and measured \(EF\) values is as follows: if \(EF\) is equal to zero, then the equation exactly describes the experimental data; if \(EF < 0.2\) then the equation describes the experimental data within experimental uncertainty; and if \(EF > 0.2\) then the equation predicts values that are different from the experimental measurements.

Figure 1 shows that the carbon-independent parameters for the \(D_0\) and \(Q\) values used in Eqs. (2) to (7) lead to predictions with \(EF\) values outside of the acceptable range for wide variations in carbon concentrations. The predicted results shown by Eqs. (4) and (5) in Table 1 are too low with \(EF\) values greater than 0.9. The critical limitation on the use of the constant parameters produces a constant carbon diffusivity for different carbon concentrations at the same temperature; thus the observed horizontal distributions in measured diffusivities shown in Fig. 1. Figure 2 shows the carbon diffusivity predicted by Eqs. (8) to (12) in Table 1, which have carbon-dependent parameters for \(D_0\) and \(Q\). These equations provide more accurate predictions than Eqs. (2) to (7) in Table 1. All correlations show acceptable \(EF\) values of 0.17 or less, which are better than the predictions in Fig. 1. These results support the importance of
incorporating carbon concentration into equations for carbon diffusivity.

Each of Eqs. (8) to (12) in Table 1 were individually developed using only a partial selection of the experimental data referenced in Table 2. In contrast, the whole body of measured data was used to obtain the two parameters for the $D_0$ and the $Q$ as a function of carbon concentration in the present study. The equation obtained from regression by using the total data set is:

$$D(T,C) = (0.146 - 0.036C) \cdot \exp \left\{ \frac{144.3 - 15.0C + 0.37C^2}{R_gT} \right\}$$

where $C$ is the carbon content in mass percent, $R_g$ is the gas constant (with units of kJ/mol-K), and $T$ is the absolute temperature (with units of K). Figure 3 shows the carbon diffusivity predicted from Eq. (14). The narrow distribution matched with experimental data and an $EF$ value of 0.129 indicates that the new expression more accurately predicts carbon diffusivity in austenite for a wide carbon concentration range. Even though Eq. (10) shows the smallest $EF$ value of 0.122, Eq. (9) consists of a larger number of parameters related to carbon content. Figure 4 shows the variation of the carbon diffusivity at different temperatures as determined by Eqs. (10), (12), and (14). All three equations predict relatively similar changes in carbon diffusivity in austenite as a function of carbon content of the iron-carbon binary system. The difference in the carbon diffusivities predicted by each equation is increased at higher temperatures.

2.2. Equation for Fe–M–C Alloys

It has been reported that the effects of alloying elements on carbon diffusion in austenite are negligible when the
amount of additional alloying elements is very small. However, as illustrated in multiple studies, alloy additions do alter carbon diffusion in austenite. Blanter (as cited in Krishtal) evaluated the effects of systematic modifications to ternary Fe–M–C alloys. Table 3 summarizes the temperature and chemical composition ranges for the ternary alloys investigated by Blanter. Krishtal also evaluated the effects of systematic modifications to ternary Fe–M–C alloys.

Table 3. Temperature and chemical composition ranges for the ternary alloys investigated by Blanter.

| Temperature Range (°C) | Carbon Range (mass pct.) | Ref. |
|------------------------|--------------------------|------|
| 927–1100               | 0.1                      | 5    |
| 750–1300               | 0.005–1.75               | 9    |
| 1000                   | 0.2–1.3                  | 11   |
| 800–1250               | 0.1–1.0                  | 13   |
| 802–1000               | 0.13–1.33                | 14   |

Fig. 2. Predicted diffusivity of carbon compared with experimental data referenced in Table 2. The diffusivity coefficient and the activation energy vary with carbon content for the equations from Table 1 used in this figure: (a) Eq. 8, (b) Eq. 9, (c) Eq. 10, (d) Eq. 11, and (e) Eq. 12.

Table 2. Experimental Conditions used for Carbon Diffusivity Measurements in Austenite.

| Temperature Range (°C) | Carbon Range (mass pct.) | Ref. |
|------------------------|--------------------------|------|
| 927–1100               | 0.1                      | 5    |
| 750–1300               | 0.005–1.75               | 9    |
| 1000                   | 0.2–1.3                  | 11   |
| 800–1250               | 0.1–1.0                  | 13   |
| 802–1000               | 0.13–1.33                | 14   |

Fig. 3. Diffusivity of carbon predicted by Eq. (14) compared with experimental data.
ated the effects of alloying elements on carbon diffusion in austenite by considering experimental data for ternary and quaternary Fe–C–based alloys. Wada et al.\textsuperscript{15–17} and Zhukov and Krishtal\textsuperscript{18} investigated the effects of alloying elements on the activity of carbon and the coefficient of carbon diffusivity for ternary Fe–M–C alloys by using thermodynamic calculations correlated with experimental data. Goldstein and Moren\textsuperscript{20} studied the influence of cross-diffusion coefficients on carbon diffusion by the additional alloying elements in a simulated carburizing process. They showed that Cr additions retarded carbon diffusion in a Fe–C–Cr alloy. Rowan and Sisson\textsuperscript{4} reported the effect of alloying elements on the diffusivity of carbon for heat-treatable low alloy steels. Their experimental analysis of alloying element effects was in good agreement with thermodynamic calculations. However, in spite of these previous investigations, a simple empirical equation for carbon diffusion considering the effects of substitutional alloying elements has not yet been reported in the literature.

Starting with Eq. (3), an expression incorporating the effects of alloy additions on carbon diffusion was developed in two steps, based on the experimental results of Blanter (as cited in Krishtal\textsuperscript{1}). First, it was assumed that an additional term related to each alloy element could be linearly added to $D_0$ and $Q$ in Eq. (14), giving

$$D(T, M, C) = (0.146 - 0.036C + k_1M)\cdot \exp \left(\frac{-144.3 - 15.0C + 0.37C^2 + k_2M}{R_jT}\right) \text{ ... (15)}$$

where $M$ is the amount of alloy element (M) added in mass percent and $k_1$ and $k_2$ are the alloying parameters for each alloying element. Zhukov and Krishtal\textsuperscript{19} indicated that that Cr attracts C and reduces the activity of C whereas Ni repels C, resulting in an increase in C activity. Similarly, Rowan and Sisson\textsuperscript{5} found that additions of Ni, which is an austenite-stabilizer, and Si, which is a ferrite stabilizer, increase the carbon diffusivity in austenite. Additions of carbide-forming elements such as Cr and Mo, on the other hand, decrease the carbon diffusivity by attracting C atoms. The addition of Cr, which is known as a strong carbide-formation element, significantly retards carbon diffusion because of the attractive interaction between Cr and C atoms.\textsuperscript{20} Thus, a cross correlation term is needed to account for the interaction of Cr and C. In Eq. (15) the $k_iM$, where $M$ is Cr is also multiplied by the carbon content, i.e., for alloys Fe–Cr–C alloys the term becomes $k_iCr$. The interaction effect between Cr and C is not considered in the $k_iCr$ term. Therefore, Eq. (15) is rearranged as the interaction of Cr and C in the pre-exponential term is distinctly considered as follows:

$$D(T, M, C) = \left(0.146 - 0.036C(1 - 1.075Cr) + k_1M\right)\cdot \exp \left(\frac{-144.3 - 15.0C + 0.37C^2 + k_2M}{R_jT}\right) \text{ ... (16)}$$

Table 3 shows the alloy concentrations that were used to determine the individual alloying parameters for each element, $k_1$ and $k_2$ in Eq. (16). Table 4 summarizes the resulting $k$-values for the eight different substitutional alloys considered by Blanter (as cited in Krishtal\textsuperscript{1}). The temperature range for the data was between 1 000 and 1 200°C. Although the pre-exponential factor in Eq. (16) indicates a slight increase in the C diffusivity with Cr, the effect of Cr on the diffusivity is dominated by the exponential factor. With a large positive $k_2$ value for Cr the overall effect of Cr is to decrease the C diffusivity and this decrease is appropriately obtained by Eq. (16).

Figure 5 correlates predicted carbon diffusivities based on just Fe–C data from Eq. (14) and by Eq. (16) with the experimental results of Blanter (as cited in Krishtal\textsuperscript{1}), and shows that for each alloy addition, Eq. (16) provides a better representation of the diffusivity data. Equation (16) shows smaller $EF$ values for all ternary Fe–M–C alloys, which is not surprising. The addition of Ni increases the diffusivity of carbon as shown in Fig. 5(c) whereas the addition of Cr decreases the diffusivity of carbon as seen in Fig. 5(b).

### 2.3. Equation for Multicomponent Steel Alloys

Following the work of Wada et al.\textsuperscript{15–17} who assert that different alloy elements affect carbon activity independently and that the interactions between two alloy elements can be ignored, Eq. (16) was modified by adding the individual contributions of each alloying element. This results in an
equation for multi-component steel alloys given by

\[
D(T,M,C) = \left(0.146 - 0.036C(1-1.075Cr) + \sum k_i M_i\right) \exp\left(-\frac{144.3-15.0C+0.37C^2 + \sum k_i M_i}{R_T T}\right)
\]

where the summation is over the alloying elements present in the steel. The same \(k_1\) and \(k_2\) given in Table 4 are used in Eq. (17). Figure 6 compares carbon diffusivities predicted by Eq. (17) with measured\(^{4,11,22,24}\) carbon diffusivities in various alloy steels. The temperature range of data used is between 850 and 1075°C. As characterized by an \(EF\) of 0.263, Fig. 6 shows reasonably good agreement between predicted diffusivities and experimental measurements. It is concluded that Eq. (17) presents a more universally applicable diffusivity expression than previously available.

It should be noted that Eq. (17) is an empirical equation

**Fig. 5.** Effect of alloy elements on the diffusivity of carbon in austenite of ternary Fe–M–C alloys: (a) Mn, (b) Si, (c) Ni, (d) Cr, (e) Mo, and (f) Al (Measured data from Blanter as cited in Krishtal\(^3\)).

**Fig. 6.** Comparison of the diffusivity of carbon predicted by Eq. (17) with the experimental data from various multi-component alloy steels.
that provides a pragmatic and computationally efficient method of calculating the diffusion of carbon in steels for the design of various heat-treatment processes. A more rigorous approach would be to obtain a compositionally-dependent equation based on the thermodynamics and kinetics of the diffusion process. Such a fundamentally based model has been derived \(^{25}\) but is computationally more complex, and in many design cases, a sound engineering approach is more than adequate. Equation (17) provides this engineering approach. Figure 7 shows the diffusivities of carbon calculated by two different methods as well as the experimental data. The carbon diffusivity calculated by the thermodynamic-based model \(^{25}\) is very close to the carbon diffusivity obtained by Eq. (17). Both sets of calculations match well with the experimental values. For the thermodynamic-based model \(^{25}\) the activity coefficient of carbon in multi-component austenite was derived thermodynamically and this activity influences the determination of the carbon diffusivity. Nevertheless, the mobility factor and the other parameters in the thermodynamic-based model \(^{25}\) related to carbon and chromium variations were optimized based on the same experimental data used in the present study. Hence, the predicted variations of the carbon diffusivity by using the empirical equation of Eq. (17) and the thermodynamic-based model \(^{25}\) are basically in correspondence.

3. Verification for Carburizing Processes

To assess the applicability of Eq. (17) to real steel alloys, a finite element (FE) analysis was used to simulate the carburizing process in low-alloy steels and predict the resulting carbon profiles for industrially significant processing histories. The commercial FE software ABAQUS \(^{26}\) was utilized with the mass diffusion subroutine incorporating Eq. (17). A one-dimensional FE analysis was conducted with a 4 mm total length and 50 μm mesh distance. Carburizing temperatures and times, as well as surface carbon potentials during gas carburizing of commercial alloys, were selected to match conditions described in the literature \(^{27,28}\) for four alloy steels: AISI 4122M, 4320H, 8620, and 9310. Table 5 summarizes the steel compositions. These steels were selected due to the availability of their published experimental carbon profiles. Figure 8 shows predictions of the FE model compared to measured carbon profiles. For each steel, the carbon diffusion described by Eq. (17), accurately predicts the experimental results. These FE simulations verify the carbon diffusivity determined by the different chemical compositions for the four low-alloy steels using Eq.

![Fig. 7. Comparison of the diffusivities of carbon calculated by both Eq. (17) and a thermodynamic-based model \(^{25}\) with the experimental data: (a) Fe–1.0Mn–xC, (b) Fe–4.0Ni–xC, (c) Fe–1.0Cr–xC, and (d) Fe–xCr–0.4C.]

![Table 5. Chemical Compositions of Experimental Carburizing Steels (mass pct.). \(^{26,27}\)]
The comparisons in Fig. 8 suggest that Eq. (17) accurately describes carbon diffusion in austenite and can be used for the design of the carburizing process and the study of austenite formation or decomposition.

To further demonstrate the importance of incorporating alloy effects on the diffusion of carbon in steels, several other simulations were performed. Figure 9 further shows the effects of the alloying elements on carbon diffusivity during the carburizing process by comparing the FE predictions of carbon profiles using three different expressions for carbon diffusivity in austenite. In addition to Eq. (17), the expression for Eq. (7) in Table 1, which assumes constant $D_0$ and $Q$ values and Eq. (14), which incorporates carbon-dependent $D_0$ and $Q$ values, were selected for this comparison. Data for the 9310 alloy shown in Fig. 8(d) were used. The carburizing process consisted of a boost step at 860°C for 71 min, followed by a diffuse step (i.e. stabilization) at 885°C for 30 min. Carbon was enriched at the surface during the boost step and was diffused into the interior during the diffuse step. As a result, the surface carbon concentration predicted by Eq. (7) in Table 1 is much lower, due to its higher carbon diffusivity, as highlighted in Fig. 9(b), an enlargement of the near-surface carbon profile. The carbon diffusivity using Eq. (17) gives good agreement with the experimental data and indicates slower carbon diffusion as compared to the other two equations, due to the effect of the alloying elements discussed in conjunction with Fig. 5. The comparison is particularly noteworthy as Eq. (17) was developed from data for ternary Fe–M–C alloys in the temperature range of 1 000 to 1 200°C, but is applied to describe diffusion data as low as the 860°C used in the boost step. Actually Eq. (17) is based on Eq. (14), which was developed for the data for the binary Fe–C alloys in the temperature range of 750 to 1 300°C.
Figure 10 shows a quantitative analysis of the effect of individual alloying elements on the carbon diffusivity in AISI 9310. Based on calculations using Eq. (17), the carbon diffusivities in the Fe–M binary alloys, with the amount of M determined from the chemical composition of AISI 9310 are compared with the carbon diffusivity in pure iron. Figure 10(a) shows that the effect of carbon concentration on carbon diffusivity in a Fe-0.11C alloy is higher than that of the pure iron, but the effect of alloy elements actually lowers the carbon diffusion in AISI 9310 when compared to pure iron. The arrows in Fig. 9(a) indicate the effect of alloying elements on the carbon diffusivity of AISI 9310 in the carburizing process. Similarly, the carbon diffusivity in a Fe-0.60C alloy is higher than that of AISI 9360 (carburized AISI 9310 as shown in Fig. 9), while both values are higher than that of the pure iron. Figure 10(b) shows the effect of each individual alloying element on the carbon diffusivity of AISI 9360. It is seen that Cr causes a large decrease in the carbon diffusivity, which more than offsets the increase caused by the carbon content. The combination of all of the alloying elements causes the difference between the carbon diffusivities. The diffusivity with the combined effect of all alloy elements is higher than that of AISI 9310 when compared to pure iron. The arrows in Fig. 9(a) indicate the effect of alloying elements on the carbon diffusivity of AISI 9310 in the carburizing process. Similarly, the carbon diffusivity in a Fe-0.11C alloy is higher than that of AISI 9360 (carburized AISI 9310 as shown in Fig. 9), while both values are higher than that of the pure iron. Figure 10(b) shows the effect of each individual alloying element on the carbon diffusivity of AISI 9360. It is seen that Cr causes a large decrease in the carbon diffusivity, which more than offsets the increase caused by the carbon content. The combination of all of the alloying elements causes the difference between the carbon diffusivities. The diffusivity with the combined effect of all alloy elements is higher than that of AISI 9310 when compared to pure iron.

4. Summary

An empirical equation (Eq. (17)) to predict carbon diffusivity in austenite as a function of chemical composition and temperature for the iron-carbon based multi-component alloy steels has been developed. The importance of the carbon concentration for the carbon diffusion was investigated by comparing previous proposed equations with experimental data. The equation developed in the present study confirms that austenite-stabilizing elements increase carbon diffusivity in austenite, while carbide forming elements decrease carbon diffusivity in austenite. Carbon profiles produced during carburizing were accurately simulated by an FE analysis that incorporated the proposed carbon diffusivity equation, which accounts for the alloy content in the steel.

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