

EXPERIMENTAL INVESTIGATION AND NUMERICAL SIMULATION OF CARBURIZATION LAYER EVOLUTION OF Cr25Ni35Nb AND Cr35Ni45Nb STEEL

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Abstract. Cr25Ni35Nb and Cr35Ni45Nb furnace tube steels, exposed to carbon-bearing environments at elevated temperature (1050-1150 °C), are susceptible to carburization attack, resulting in serious material deterioration and shortening service life. Depth of carburization layer, one of important marks of residual life for as-carburized furnace tubes, has been paid more attention frequently. In this paper, Depth growth of the carburization layer along the radial direction of Cr25Ni35Nb and Cr35Ni45Nb furnace tube was obtained by use of pack carburizing at two carburization temperature (1000 °C and 1100 °C) for different time. Then based on the Fick's second law and equilibrium constant method, a mathematical model for predicting variation of carburization layer of the two alloys above was established. The model consists of two parts: calculation of carbon diffusion based on Fick's second law and calculation of the carbide precipitation using equilibrium constant method. The results of numerical simulation are in agreement with the results of the experiments and the carburization time-dependent depth curve of carburization layer is parabolic.

1. INTRODUCTION

Cr25Ni35Nb and Cr35Ni45Nb centrifugally cast steels are widely used as ethylene cracking furnace tube for high temperature resistant properties and corrosion resistant properties. However, carburization damage often occurs during service life under high carbon potential, low oxygen partial environment, which deteriorates mechanical and microstructure properties and shorts service life of furnace tube [1-4]. The relationship between depth of carburization layer and time, as the most important symbol of predicting residual life of as-carburized furnace tube and base of investigating carburization damage, is increasingly paid attention to [5-8]. Depth of carburization layer can be investigated by calculating carbon concentration by a diffusion method and microhardness along the cross profile of as-carburized furnace tube.

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Equilibrium constant method is developed by Bongartz [5], which can be used for simulating carburization process for different alloys by calculating precipitation of different carbides, but condition of transforming between different carbides is ignored. Modified equilibrium constant method is developed by Meili Zhu et al. [9]. Transforming between $M_{23}C_6$ carbide and M_7C_3 carbide is coupled in the diffusion model, which is more appropriate for practical cases than initial diffusion model. However, the relationship between microhardness of as-carburized furnace tube and depth of carburization layer is barely reported. Therefore, in this paper, depth growth of the carburization layer along the radial direction of Cr25Ni35Nb and Cr35Ni45Nb furnace tube were obtained by measuring microhardness of as-carburized specimens through pack carburizing at two carburization temperatures

Table 1. Chemical composition of Cr25Ni35Nb and Cr35Ni45Nb steel [wt.%].

Element	C	Si	Mn	Cr	Ni	Nb	Fe
Cr25Ni35Nb	0.51	1.54	0.8	24.69	34.90	0.60	balance
Cr35Ni45Nb	0.44	1.72	0.94	31.69	42.51	0.71	balance

(1000 °C and 1100 °C). Then based on the Fick's second law and equilibrium constant method, a mathematical model for predicting of carburization layer of Cr25Ni35Nb and Cr35Ni45Nb steel was established for predicting the growth of carburization layer with time.

2. EXPERIMENTAL INVESTIGATION

2.1. Experimental procedure

Two different carburization experiments were investigated. Carbon weight gain test was performed for calculating carbon diffusion rate constant, local carburizing test was implemented for measuring microhardness along the cross profile of as-carburized specimen. Chemical composition of Cr25Ni35Nb and Cr35Ni45Nb steel (wt.%) is listed in Table 1.

For carbon weight gain test, flat specimens with size of 10 mm×10 mm×5 mm for packing carburization were cut from virgin pipes, and carbon potential a_c was supposed to 1 [10]. Grinded with 100#-800# abrasive papers, cleaned with absolute ethyl alcohol, dried, and weighed by electronic balance (0.01 mg), then the specimens were heated to 1000 °C and 1100 °C at a packing carburization container in Ceramic fiber muffle furnace for different hours.

For local carburizing test, anti-carburizing coating was sprayed on surfaces of specimen except inner surface. After being carburized for 10, 20, 30, 40, 50, 60, and 80 hrs, Vickers hardness was measured along the radial direction from inner surface.

2.2. Experimental results

2.2.1. Carbon diffusion rate constant

Carburizing kinetic curves of Cr25Ni35Nb and Cr35Ni45Nb steel at 1100 °C and 1000 °C are shown in Fig. 1. It is clearly seen from Fig. 1 that the curve is parabolic, which means that carburization process is controlled by carbon diffusion. The carbon diffusion coefficient K can be calculated by the following equation:

$$W^2 = Kt, \quad (1)$$

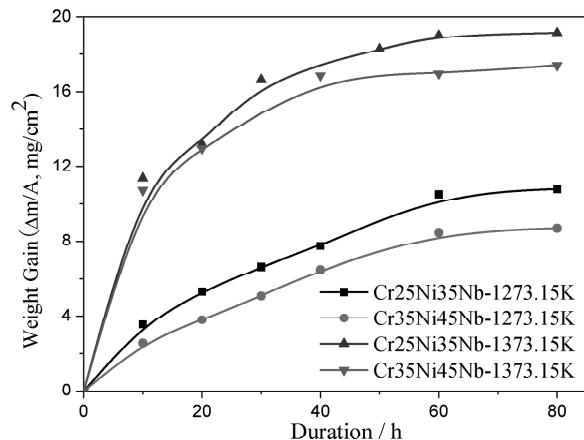


Fig. 1. Carburizing kinetic curves of the two carburized steel at 1100 °C and 1000 °C.

W is carbon weight gain per unit area/ $\text{mg} \times \text{cm}^{-2}$; t is carburization time/hour; K is carbon diffusion rate constant/ $\text{mg}^2 \times \text{mm}^{-4} \times \text{h}^{-1}$.

Table 2 shows the carbon diffusion rate constants of the two as-carburized steels at different temperatures, it is clearly seen from Table 2 that the carbon diffusion rate constants increase sharply with temperature rising. At a given temperature, the carbon diffusion rate constant of Cr35Ni45Nb steel is lower than that of Cr25Ni35Nb steel, which means that carburization resistance of Cr35Ni45Nb steel is better than that of Cr25Ni35Nb steel.

2.2.2. Depth evolution of carburization layer based on hardness test

Fig. 2 shows carburizing layer depth evolution of Cr25Ni35Nb and Cr35Ni45Nb steel at 1000 °C and 1100 °C based on Vickers hardness test. From the results of the hardness test, depth of decarburizing layer increases with time increasing. The curves of depth variation of carburizing layer are parabolic, which are similar to carburizing kinetic curves.

Table 2. Carbon diffusion rate constants of Cr25Ni35Nb and Cr35Ni45Nb steel.

Material	Carbon diffusion rate constant	
	1000 °C	1100 °C
Cr25Ni35Nb	1.57×10^{-4}	5.81×10^{-3}
Cr35Ni45Nb	1.01×10^{-4}	4.74×10^{-3}

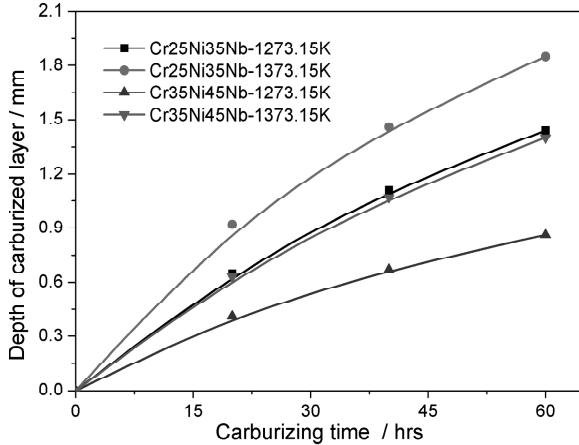


Fig. 2. Depth evolution of carburizing layer of the two carburized steel based on hardness tests.

3. NUMERICAL SIMULATION OF CARBON DIFFUSION

3.1. Theoretical model

Carburization is a diffusion-control process, mathematic model of which is composed of diffusion calculation and carbide precipitation calculation. Alternation and iterative algorithm is applied in the two calculation process: the first step is used for calculating carbon diffusion, which is based on the Fick's second law. The time and space is discretized by using finite difference method; the second step is based on equilibrium constant method, and is applied for carbide precipitation by using the chemical reaction equilibrium constant. In order to acquire the distribution of carbon concentration, chemical composition, initial and boundary conditions, carbon diffusion coefficient at different temperature, molecular formulas of precipitated carbides, equilibrium constants of carbides and activity coefficient are needed.

3.1.1. Calculation of carbon diffusion

The model for calculating carbon diffusion is based on the Fick's second law, for carbon diffusion is investigated in furnace tube, diffusion is considered along the radial direction x , which can be written as:

$$D \cdot \frac{\partial^2 C}{\partial x^2} + D \cdot Z \cdot \frac{\partial C}{\partial x} = \frac{\partial C}{\partial t}, \quad (2)$$

D is the diffusion coefficient of the carbon in solution, t is the time and C is the carbon concentration. D is assumed to be constant in this paper. Z is the factor of geometry: 0-plane geometry,

1- cylindrical geometry, 2- spherical geometry. For the furnace tube, Eq. (2) can be simplified as:

$$\frac{\partial C}{\partial t} = D \left(\frac{\partial^2 C}{\partial x^2} + \frac{1}{x} \frac{\partial C}{\partial x} \right). \quad (3)$$

Eq.(2) can be discretized by finite difference. A two dimensional grid of space / time in x and t is established. Δx is set as space increment, and Δt is set as time increment. The concentration $C(x, t)$ is transformed to $C(i, j)$. As a result, the basic working equation of the model is acquired:

$$C(i, j+1) = U(i) \cdot C(i-1, j) + V \cdot C(i, j) + W(i) \cdot C(i+1, j), \quad (4)$$

where

$$U(i) = \frac{D}{2} \frac{\Delta t}{\Delta x} \left(\frac{2}{\Delta x} - \frac{1}{x_i} \right), \quad V = 1 - \frac{2D\Delta t}{\Delta x^2}$$

and

$$W(i) = \frac{D\Delta t}{2\Delta x} \left(\frac{2}{\Delta x} + \frac{1}{x_i} \right).$$

3.1.2. Calculation for precipitation of carbides

Two basic assumptions for calculating precipitation of carbides by using equilibrium constant are as following: (1) rate of nucleation and growth for carbide is faster than rate of carbon diffusion; (2) nucleation of carbide is uniform, and prior nucleation of carbide at boundary is ignored. These assumptions are reasonable for the steel which has high content of carbide forming element [6].

For Cr25Ni35Nb and Cr35Ni45Nb steels, MC, $M_{23}C_6$, and M_7C_3 (M is metal element) carbides precipitate in carburization process, whose chemical composition is similar to NbC, $Cr_{16}Fe_7C_6$, and $Cr_{3.5}Fe_{3.5}C_3$ carbide respectively [7,8]. Carbon exists in austenitic matrix and carbide, and only the former can further diffuse and precipitate.

For the carbide NbC, the chemical reaction for carbide formation is assumed as Eq. (5a). Carbon concentration of the matrix N_{c1} that is equilibrium with the carbide $M_{23}C_6$ calculated based on Eq. (5a) can be expressed as Eq. (5b), and relationship of solubility parameter K_{s1} of NbC with equilibrium constant K_{p2} can be expressed Eq. (5c):



$$N_{c_1} = \frac{1}{N_{Nb} \cdot K_{s1}}, \quad (5b)$$

$$K_{s1} = \frac{1}{N_c \cdot N_{Nb}} = K_{p1} \cdot \gamma_c \cdot \gamma_{Nb}. \quad (5c)$$

For $M_{23}C_6$ and M_7C_3 , N_{c2} , K_{s2} , N_{c3} , K_{s3} can be expressed as:

$$N_{c2} = \frac{1}{K_{s2}^{1/6} \cdot N_{Cr}^{16/6} \cdot N_{Fe}^{7/6}}, \quad (6a)$$

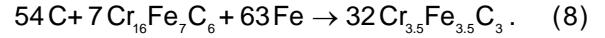
$$K_{s2} = \frac{1}{N_c^6 \cdot N_{Cr}^{16} \cdot N_{Fe}^7} = K_{p2} \cdot \gamma_c^6 \cdot \gamma_{Cr}^{16} \cdot \gamma_{Fe}^7, \quad (6b)$$

$$N_{c3} = \frac{1}{K_{s3}^{1/3} \cdot N_{Cr}^{3.5/3} \cdot N_{Fe}^{3.5/3}}, \quad (7a)$$

$$K_{s3} = \frac{1}{N_c^3 \cdot N_{Cr}^{3.5} \cdot N_{Fe}^{3.5}} = K_{p3} \cdot \gamma_c^3 \cdot \gamma_{Cr}^{3.5} \cdot \gamma_{Fe}^{3.5}. \quad (7b)$$

N_{c1} , N_{c2} , and N_{c3} is the mole fraction of carbon of matrix those are equilibrium with the carbides MC , $M_{23}C$, and M_7C_3 ; γ_{Cr} , γ_{Fe} , and γ_c is the activity coefficient of Cr, Fe, C, in austenite respectively; N_{Cr} , N_{Fe} , and N_c is the mole fraction of Cr, Fe, C at austenite respectively; K_{p1} , K_{p2} , and K_{p3} is the equilibrium constant of chemical reaction for forming carbides of NbC , $Cr_{16}Fe_7C_6$, and $Cr_{3.5}Fe_{3.5}C_3$ respectively.

The parameters N_{c1} , N_{c2} , and N_{c3} are firstly changed into mass fraction C_1 , C_2 , C_3 and $C_1 < C_2 < C_3$. $C(t_2)$ is the carbon concentration at any time t_2 , which can be calculated by Eq. (3). If $C(t_2) < C_i$ ($i = 1, 2, 3$), the carbide will precipitate. In this paper, when $C(t_2) < C_1$, carbide does not precipitate; when $C_1 < C(t_2) < C_2$, the carbide NbC will precipitate; when $C_2 < C(t_2) < C_3$, the carbide $Cr_{16}Fe_7C_6$ will precipitate; when $C_3 < C(t_2)$, the carbide $Cr_{16}Fe_7C_6$ will change into $Cr_{3.5}Fe_{3.5}C_3$ according to Eq. (8). If $Cr_{16}Fe_7C_6$ fully changes into $Cr_{3.5}Fe_{3.5}C_3$, the carbide $Cr_{3.5}Fe_{3.5}C_3$ will precipitate directly. The criteria of $Cr_{16}Fe_7C_6$ fully changing into $Cr_{3.5}Fe_{3.5}C_3$ is the concentration of Fe in the matrix, which is based on the theory of Zhu et al. [9]. When some carbide precipitates, the extra carbon $\Delta C(t_2) = C(t_2) - C(t_2)$ will be set as the carbon which exists in the carbide, and then the loss amount of Fe and Cr for forming carbide will be calculated according to the chemical reaction equation, finally current concentration of each element in the matrix will be calculated for the next step.



3.2. Definition of boundary conditions

The content of carbide forming element in the matrix has change for precipitated carbides existing during manufacture. The initial value of each element must be calculated before carbon diffusion, the losing element for forming carbide should be deducted. Initial carbon concentration of the matrix at $t=0$:

$$C|_{t=0} = C_0. \quad (9)$$

Inner boundary condition: initial carbon concentration of the matrix where is far from the surface for carbon diffusion.

$$C|_{r=\infty} = C_0. \quad (10)$$

Outer boundary condition: diffusion flux of carbon diffusion can be expressed as the following Eq. (11), which is equal to the value of carbon weight gain per unit area and per unit time.

$$J = -D \frac{\partial C}{\partial x} \Big|_{x=R_i} = \frac{\partial W}{\partial t}, \quad (11)$$

R_i -Inner radius of furnace tube; W - value of carbon weight gain unit area, which is be related to time.

3.3. Calculation of carbon diffusion mode parameters

In order to calculate the diffusion and precipitation process, the thermodynamic and kinetic date is necessary. According to the theory of chemical equilibrium, equilibrium constant for forming carbide can be calculated by free enthalpy of precipitated carbide.

$$K_{p(M_xC_y)} = \exp \left(-\frac{\Delta G^0}{RT} \right), \quad (12)$$

ΔG^0 is Gibbs free enthalpy of chemical reaction; R is gas constant; T is Kelvin temperature. The value of ΔG^0 for forming carbides of NbC , $Cr_{16}Fe_7C_6$, and $Cr_{3.5}Fe_{3.5}C_3$ can be expressed as:

$$\Delta G_{NbC}^0 = -130000 + 1.77T[J/mol], \quad (13)$$

$$\Delta G_{Cr_{16}Fe_7C_6}^0 = -304300 - 76.6T[J/mol], \quad (14)$$

$$\Delta G_{Cr_{3.5}Fe_{3.5}C_3}^0 = -72500 - 36.5T[J/mol]. \quad (15)$$

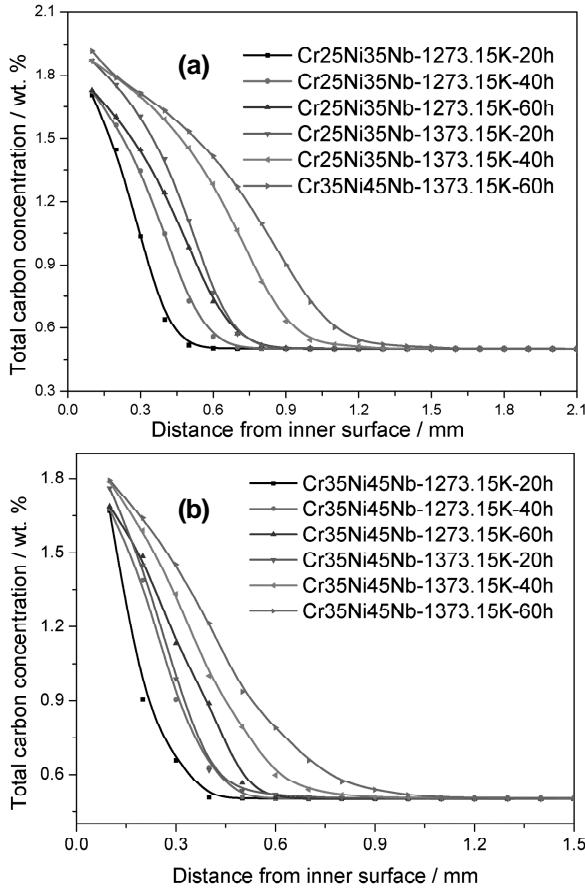


Fig. 3. Total carbon concentration of as-carburized Cr25Ni35Nb and Cr35Ni45Nb steel: a) Cr25Ni35Nb; b) Cr35Ni45Nb.

According to the theory of K. Natesan et al. [10] and E.Schurmann et al. [11], in the temperature range 850 °C to 1150 °C, activity coefficient of Nb, Fe, Cr, and C can be calculated respectively as: $\gamma_{\text{Nb}} = 0.1$, $\gamma_{\text{Fe}} = 1$, $\gamma_{\text{Cr}} = 2.3$, $\gamma_{\text{C}} = 20$. Based on the above data and Eq. (5c), Eq. (6b), and Eq. (7b), solubility parameters for carbide of MC, $M_{23}C_6$ and M_7C_3 at 1000 °C and 1100 °C are achieved.

4. RESULTS AND DISCUSSION

Fig. 3a and Fig. 3b shows the total carbon concentration of as-carburized Cr25Ni35Nb and Cr35Ni45Nb steel at different carburizing temperatures for 20, 40, 60 hours respectively. For the two as-carburized steels, it is clearly concluded that the value of total carbon concentration is maximum at the inner surface of furnace tube, and decreases with distance increasing from the inner surface. With carburizing time increasing, the value of total carbon concentration and depth of carburization layer increases. Compared to Cr25Ni35Nb steel, at a given carburizing time, the total carbon concentration of as-carburized Cr35Ni45Nb steel is lower, which again

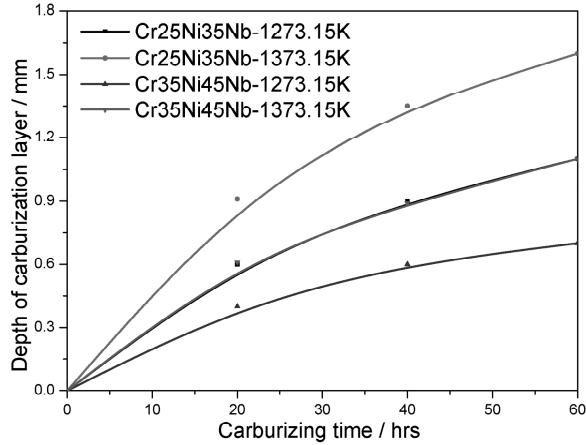


Fig. 4. Depth variation of carburizing layer of the two carburized steel based on simulated test.

certifies that carburization resistance of Cr35Ni45Nb steel is better than that of Cr25Ni35Nb steel, and this is in conformity with practical condition.

Fig. 4 shows the depth evolution of carburization layer with time increasing for as-carburized Cr25Ni35Nb and Cr35Ni45Nb steel at different temperature. It is summarized that depth evolution curves of Cr25Ni35Nb and Cr35Ni45Nb steel are parabolic. Although depth evolution tendency of carburization layer of experimental results and numerical simulated results for Cr25Ni35Nb and Cr35Ni45Nb steel are similar, but deviation exists between the experimental result and numerical simulated result, the deviation value is given in Fig. 5. For a given material and carburizing temperature, the variation value increases with time increasing, this is caused by various factors. In this paper, simulative conditions are simplified. The diffusion coefficient D is assumed to be constant during the car-

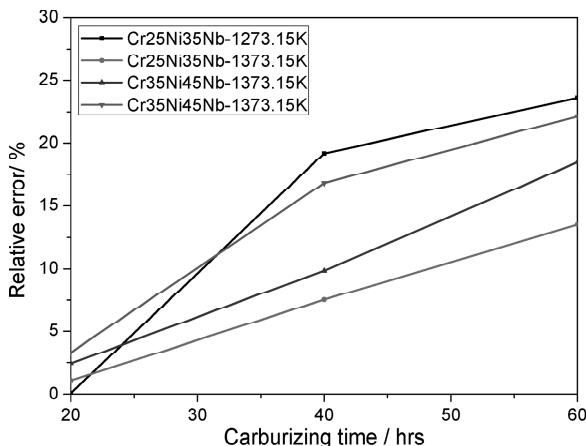


Fig. 5. Relative error values between experimental results and simulated results.

burizing process, which varies actually due to chemical composition variation of austenitic matrix for precipitated carbides. Meanwhile, activity coefficients of alloy elements are from literatures and are assumed to be constant, which are not sufficiently reasonable. Based on the above reasons, the numerical simulated results are generally lower than of experimental results.

Preferable carburization resistance of Cr35Ni45Nb steel is depended on higher content of Cr and Ni. Cr and Ni content in Cr35Ni45Nb steel is increased by 10%. Ni is a non-carburizing forming element for generating and stabilizing austenitic matrix at high temperature, which decreases solubility of carbon at austenitic matrix and increases carburization and oxidation resistance. The optimum carburization resistance is achieved at Ni/Fe=4/1 (wt.), where the carbon diffusion and solubility shows the minimum [1]. The value is lower or higher than 4, diffusion and solubility value of carbon increases. Value of Ni/Fe in Cr35Ni45Nb steel is higher than that in Cr25Ni35Nb steel, meanwhile which is lower than 4. Therefore, Cr35Ni45Nb steel has higher carburization resistance.

5. CONCLUSION

(1) Based on the Fick's second law and equilibrium constant method, depth growth of the carburization layer along the radial direction of Cr25Ni35Nb and Cr35Ni45Nb furnace tube are investigated by use of pack carburizing at two carburization temperature (1000 °C and 1100 °C) for different carburizing time. The numerical simulated results are in agreement with the experimental results.

(2) The carburization time-dependent depth curve of carburization layer is parabolic, which is similar to carbon kinetics curve, this means that carburization is diffusion-control.

(3) From the numerical simulated results and experimental results, it is clearly concluded that carburization resistance of Cr35Ni45Nb steel is higher than that of Cr25Ni35Nb steel. Preferable carburization resistance is due to higher content of Cr and Ni.

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