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Kinetics of Carbide Layer Forming on the Surface of Steel in Molten Systems

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Abstract: A mathematical model of kinetics of carbide layer formed on the surface of steel in fused system was set up with the theory of non-stable diffusion mass transfer and regular solution sub-lattice. This model was analyzed and testified by the experiments in which the VC layers were formed on four kinds of steels as steel 45 ,4Cr5MoSiV1,T10, and Cr12MoV immersed in the $V_2O_5-Na_2O-B_2O_5$ fused system with the reducing agent of silicon .The results showed that there was a good agreement between the model and the experimental results ;the growth speed of carbide layer depended on the factors of carbon activity in substrate, treatment temperature ,kinds of carbides and its structure etc.

Key words: fused system, carbide, layer treatment, kinetics

The carbides of the transitional metal, which belong to the type of metal-like carbides, have high melting points, high hardness, high chemical stability and excellent electric conductivity. The carbide layer with certain thickness can improve the surface hardness, wear resistance, corrosion-resistance and oxidation-resistance of steel ,and its development and application have been drawn extensive attentions. This carbide layer forming technique on the surface of steel in the fused system is an important means of the formation of carbide layer, with characteristics of simple equipment, low cost, dense layer and strong bondage. The experiments by Aria etc. showed that[1~3], the process of the carbide layer forming under this condition was controlled by diffusion of carbon, the thickness of layer was proportional to the square root of the treatment time, and the high carbon content facilitates conducive to the increase of the layer forming speed. However, the proper relationship between them was not indicated clearly in the papers; The simplified model of the layer growth based on the theory of stable diffusion did not conform ideally to the experimental results[4] . In this paper, the mathematical model on the kinetics of the carbide layer growth was set up, which was based on the theory of non-stable diffusion mass-transfer and regular solution sub-lattice. By comparison of this model with the experimental results in case of VC layer, the relationship between the layer growth and factors of carbon diffusion drive, carbon content in steel ,activity and temperature etc. is analyzed.

1 Materials and Methods

In this experiment, four kinds of steels of 45, 4Cr5MoSiV1,T10 and Cr12MoV were taken as the substrate material to be coated .Their chemical compositions are shown in table 1, where y_i is the mole fraction of the components on their own sub-lattice.All four materials were tempered at high temperature, made into the sample with size of 12 mm × 12 mm × 20 mm, fine polished with 900# water abrasive paper and degreasing before VC layer forming treatment.

This VC layer forming treatment was performed in SG7.5- 1300 crucible type resistance furnace. The fused system of $V_2O_5-Na_2O-B_2O_5$ was made in the heat resistance steel crucible sized ϕ 110 mm × 240 mm with Si powder as reducing agent.After attaining the predetermined temperature, the sample was put into the fused system ,with the treatment temperature at 850, 950, 1 000℃, and time of 1, 2, 4, 8 and 16 h. After that, the samples were quenched in oil, cleaned with boiling water, cross-sectioned and made into the microscopic sample. The thickness of layer was measured after being itched with 4% nital, and the average of the values measured at ten spots on each of four samples under same treatment condition was taken as the experimental results.

Table 1 Chemical compositions and activities of the materials

Element	Front of the layer		45		4Cr5MoSiV		T10		Cr12MoV	
	x_i	y_i	w/%	y_i	w/%	y_i	w/%	y_i	w/%	y_i
C	0.428 6	0.750 0	0.43	0.020 0	0.34	0.015 6	1.02	0.050 4	1.40	0.065 4
Si	–	–	0.24	0.004 8	0.84	0.016 6	0.31	0.006 2	0.22	0.004 4
Mn	–	–	0.58	0.005 9	0.35	0.003 6	0.28	0.002 8	0.48	0.004 9
Mo	–	–	–	–	1.20	0.006 9	–	–	1.00	0.005 9
V	0.571 4	1.000 0	–	–	1.05	0.011 4	–	–	0.35	0.003 8
Cr	–	–	–	–	5.14	0.054 8	–	–	12.58	0.135 9
a_C 850℃	$0.260\,5\times10^{-3}$		0.336 6		0.107 6		1.049 1		0.249 9	
a_C 900℃	$0.417\,3\times10^{-3}$		0.271 4		0.093 1		0.840 2		0.234 7	
a_C 950℃	$0.629\,1\times10^{-3}$		0.222 6		0.081 4		0.685 3		0.221 6	
a_C 1 000℃	$0.927\,7\times10^{-3}$		0.185 6		0.072 1		0.567 9		0.210 2	

2 Experimental Results

The results of the experiment were shown in Fig. 1 and Fig. 2. The relationship between the thickness of carbide layer and treatment temperature for each steel treated for 4 h was shown in Fig. 1. The result showed that the thickness of VC layer increases dramatically with the increase of treatment temperature. In Fig. 2 shows the relationship between thickness of VC layer and the treating time, for different substrates of steels appears the same trend in the figure, i.e. the thickness of layer is proportional to the square root of the treating time. Generally speaking, this relationship showed that the growth speed of VC layer is controlled by the volume diffusion of carbon atom.

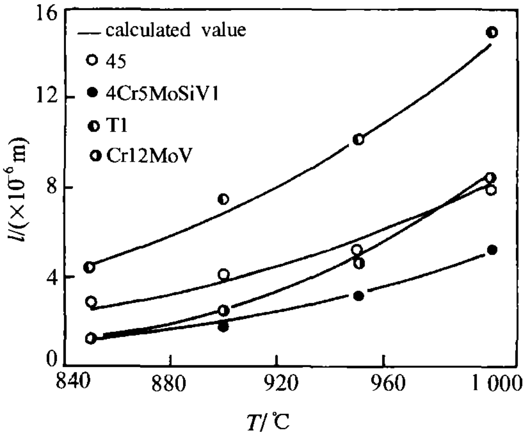

Fig.1 Relation between VC layer thickness(l) and treating temperature (t = 4 h)

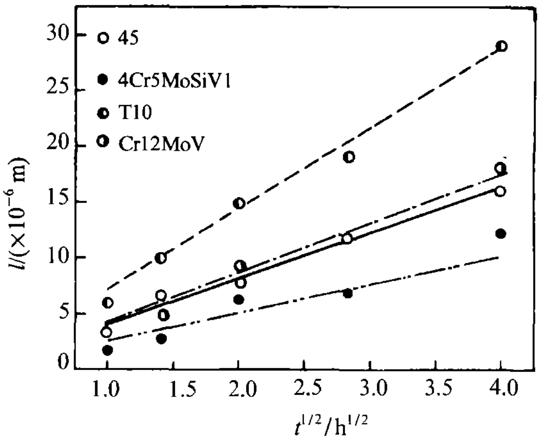

Fig.2 Relation between VC layer thickness (l) and treting time (T=1 000℃)

3 Kinetics of Growth of Carbide and Analysis of the Experimental Results

3.1 Analysis of experimental results

The dissolved atoms of carbide forming element (e.g. V, Ta, Zr, Nb, Cr, Ti, etc.) are reduced in the fused system, through diffusion and adhesion, combined with the carbon atom forming the carbide at the surface of the material to be coated. The growth is maintained by the continual diffusion of carbon atom in the substrate through the substrate and formes carbide layer, with certain thickness. At the processing temperature, the activation energy of the chemical reaction was far smaller than the diffusion activation energy, the diffusion coefficient of the carbon atom in the carbide was far less than that in the austenite substrate, and less than that of the dissolved atom of CFE in the fused system. So the process of layer formation is controlled by diffusion of the carbon atom in the carbide layer.

The composition of transitional metal carbide may be changeable in a certain range, it is a homogeneous phase in certain scope of carbon content, similar to the vacancy solid solution[4], and this is vital to growth of the carbide layer. The difference of the carbon concentration between the inner and outer layer makes certain activity gradient, just like calculated results for VC layer with model of regular solution sub-lattice described later in this paper, the carbon activity is less than 10^{-3} when carbon content is at the lower limit in the varied scope (e.g. x_C= 0.428 6 ,mole fraction) ; by contrast, the carbon activity will attain 1.00 (e.g. x_C =0.499 5, a_C=1.00) when the carbon content is near to the upper limit. This activity difference is an important kinetic factor for the diffusion of the carbon atom through the carbide layer.

The mass transfer of carbon in the carbide is of non-stable diffusion. So the following hypothesis on basis of the above analysis can be made: the activity and concentration distribution can be expressed with the error function, carbon is distributed evenly in the austenite substrate; during the process of the layer growth, the concentration and activity of carbon in austenite substrate, at the interface of the layer and substrate, and at the front of the layer remain constant. The model of the carbide layer growth set up accordingly was shown in Fig.3 for 45 steel.

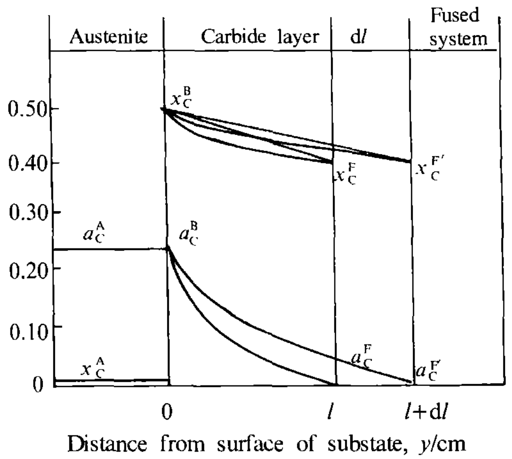

Fig.3 Distribution of carbon concentration and activity and model of growth of carbide layer

When carbon atoms attain local kinetic equilibrium between in the carbide and in austenite substrate, the carbon activity equals at the interface, i.e. $a_C^A = a_C^B$. The carbon concentration near the substrate approaches the upper limit of the carbon content in the homogeneous carbide phase; at the front of the layer, the concentration of carbon equals to the lower limit. For VC layer, $x_C^B \approx 0.5, x_C^{F'} = x_C^F = 0.428\,6$.

3.2 Kinetics equation of growth for carbon layer

Given that the distribution of the carbon activity in the layer as follows

$$a_C = p + q \cdot \mathrm{erf}(y / \sqrt{4D_C t}) \qquad (1)$$

According to the boundary conditions

$$y = 0, a_C = a_C^B = a_C^A = p + q \cdot 0 = p$$
$$y = l, a_C = a_C^F = p + q \cdot \mathrm{erf}(l / \sqrt{4D_C t}) \qquad (2)$$

The values of p and q acquired are substituted in Eq. (1), then the distribution equation of carbon activity in the layer is

$$a_C = a_C^A - (a_C^A - a_C^F)\frac{\mathrm{erf}(y / \sqrt{4D_C t})}{\mathrm{erf}(l / \sqrt{4D_C t})} \qquad (3)$$

The gradient of the carbon activity near the substrate in the layer is

$$\left.\frac{\mathrm{d}a_C}{\mathrm{d}y}\right|_{y=0} = -\frac{a_C^A - a_C^F}{\sqrt{\pi D_C t} \cdot \mathrm{erf}(l / \sqrt{4D_C t})} \qquad (4)$$

Given that when treating time t' equals to t, the thickness of layer y is l; when t equals to t+dt, y equals to l+dl. Part of the carbon atoms diffused from the substrate to the layer contributes to the growth of layer, and the left is used to increase the carbon content in the layer. As shown in Fig.3, it is suitable to estimate the area enclosed by the three curves of $\overline{x_C^B x_C^F}$, $\overline{x_C^B x_C^{F'}}$ and $\overline{x_C^F x_C^{F'}}$ with the area of the triangle $\Delta x_C^B x_C^F x_C^{F'}$.

According to mass balance principle, we have

$$\left.\frac{\mathrm{d}a_C}{\mathrm{d}y}\right|_{y=0} \cdot \frac{D_C \cdot A \cdot \mathrm{d}t}{V_m} = \frac{A \cdot x_C^F \cdot \mathrm{d}l}{V_m} + \frac{A \cdot (x_C^B - x_C^F)}{2V_m}\mathrm{d}l \qquad (5)$$

where A is the area of the layer, cm^2; V_m is volume of the carbide possessed by one mole of carbide in average, cm^3/mol ; D_C is the diffusion coefficient of carbon atom in the carbide, cm^2/s. Bring eqation (4) into eqation(5) , noticing that when Z is small, the mathematical approximation of $\mathrm{erf}(Z) \approx 2Z / \sqrt{\pi}$ is correct, then the above equation is simplified as :

$$2D_C \cdot \frac{a_C^A - a_C^F}{x_C^B + x_C^F} \cdot \mathrm{d}t = l \cdot \mathrm{d}l \qquad (6)$$

Integrate on both sides of the above equation for t and l in the range of 0~t and 0~l respectively, then

$$l^2 = 4D_C \cdot \frac{a_C^A - a_C^F}{x_C^B + x_C^F} \cdot t \qquad (7)$$

this is the kinetics equation of growth for single phase carbide layer.

In equation (7), the carbon activity a_C^A in the austenite substrate and a_C^F at the front of the carbide layer are both defined with the pure graphite as standard state

$$\left.\begin{aligned} G_{\mathrm{C}}^{\mathrm{MC}} &= {}^{\ominus}G_{\mathrm{C}}^{\mathrm{gr}} + RT\ln a_{\mathrm{C}}^{\mathrm{F}} \\ G_{\mathrm{C}}^{\mathrm{A}} &= {}^{\ominus}G_{\mathrm{C}}^{\mathrm{gr}} + RT\ln a_{\mathrm{C}}^{\mathrm{A}} \end{aligned}\right\} \tag{8}$$

Where $G_{\mathrm{C}}^{\mathrm{MC}}$ and $G_{\mathrm{C}}^{\mathrm{A}}$ are chemical potential of the carbon in the carbide layer and in austenite substrate respectively, ${}^{\ominus}G_{\mathrm{C}}^{\mathrm{gr}}$ is standard mole Gibbs free energy of pure graphite.

The austenite and carbon are cavity solid solution or cavity compound. Therefore the model of regular solution-sub lattice proposed by M. Hillert[5] can make up the shortcomings exposed by regular solution model used for cavity phase. The chemical potentials of carbon in the austenite and in the carbide layer obtained according to this model are as follows respectively:

$$G_{\mathrm{C}}^{\mathrm{A}} = {}^{\ominus}G_{\mathrm{FeC}}^{\mathrm{A}} - {}^{\ominus}G_{\mathrm{Fe}}^{\mathrm{A}} + L_{\mathrm{CV}}^{\mathrm{A}}(1 - 2y_{\mathrm{C}}^{\mathrm{A}}) + RT\ln[y_{\mathrm{C}}^{\mathrm{A}} / (1 - y_{\mathrm{C}}^{\mathrm{A}})] + \sum_{i=2}^{N} J_i^{\mathrm{A}} y_i^{\mathrm{A}} \tag{9}$$

$$G_{\mathrm{C}}^{\mathrm{MC}} = ({}^{\ominus}G_{\mathrm{M}_m\mathrm{C}_n}^{\mathrm{MC}} - m\,{}^{\ominus}G_{\mathrm{M}}^{\mathrm{MC}}) / n + (1 - 2y_{\mathrm{C}}^{\mathrm{MC}}) + RT\ln[y_{\mathrm{C}}^{\mathrm{MC}} / (1 - y_{\mathrm{C}}^{\mathrm{MC}})] \tag{10}$$

where ${}^{\ominus}G_{\mathrm{FeC}}^{\mathrm{A}}$ and ${}^{\ominus}G_{\mathrm{Fe}}^{\mathrm{A}}$ are standard mole Gibbs free energy for austenite cavity sub-lattice wholly occupied by carbon atom and all vacancy (i.e. austenite pure iron) respectively, J/mol; ${}^{\ominus}G_{\mathrm{M}_m\mathrm{C}_n}^{\mathrm{MC}}$ and ${}^{\ominus}G_{\mathrm{C}}^{\mathrm{MC}}$ are mole free energy of carbide with chemical constitution of $\mathrm{M}_m\mathrm{C}_n$ and of pure metal M with the same structure as carbides respectively, J/mol; $y_{\mathrm{C}}^{\mathrm{A}}$ and y_i^{A} are mole fraction of carbon and alloy atom on their own sub-lattice in the austenite respectively; $y_{\mathrm{C}}^{\mathrm{MC}}$ is mole fraction of carbon atom on its sub-lattice in the carbide at the front of the layer; $L_{\mathrm{CV}}^{\mathrm{A}}$ and $L_{\mathrm{CV}}^{\mathrm{MC}}$ are the reactive energy between carbon atom and vacancy on cavity sub lattice of austenite and carbide respectively, J/mol; J_i^{A} is the coefficient affecting the carbon activity of the alloy element in austenite substrate , J/mol.

From eqations (8) to (10), expression of the carbon activity in austenite substrate and at the front of carbide layer can be obtained as follows

$$a_{\mathrm{C}}^{\mathrm{A}} = \frac{y_{\mathrm{C}}^{\mathrm{A}}}{1 - y_{\mathrm{C}}^{\mathrm{A}}} \exp\frac{1}{RT}[{}^{\ominus}G_{\mathrm{FeC}}^{\mathrm{A}} - {}^{\ominus}G_{\mathrm{Fe}}^{\mathrm{A}} - {}^{\ominus}G_{\mathrm{C}}^{\mathrm{gr}} + L_{\mathrm{CV}}^{\mathrm{A}}(1 - 2y_{\mathrm{C}}^{\mathrm{A}}) + \sum_{i=2}^{N} J_i^{\mathrm{A}} y_i^{\mathrm{A}}] \tag{11}$$

$$a_{\mathrm{C}}^{\mathrm{F}} = \frac{y_{\mathrm{C}}^{\mathrm{MC}}}{1 - y_{\mathrm{C}}^{\mathrm{MC}}} \exp\frac{1}{RT}[\frac{1}{n}({}^{\ominus}G_{\mathrm{M_mC_n}}^{\mathrm{MC}} - m \cdot {}^{\ominus}G_{\mathrm{M}}^{\mathrm{MC}} - (n \cdot {}^{\ominus}G_{\mathrm{C}}^{\mathrm{gr}}) + L_{\mathrm{CV}}^{\mathrm{MC}}(1 - 2y_{\mathrm{C}}^{\mathrm{MC}})] \tag{12}$$

3.3 Comparison between kinetics equation and experimental results

The group of $({}^{\ominus}G_{\mathrm{FeC}}^{\mathrm{A}} - {}^{\ominus}G_{\mathrm{Fe}}^{\mathrm{A}} - {}^{\ominus}G_{\mathrm{C}}^{\mathrm{gr}})$ in equation (11) and group of $({}^{\ominus}G_{\mathrm{M_mC_n}}^{\mathrm{MC}} - m \cdot {}^{\ominus}G_{\mathrm{M}}^{\mathrm{MC}} - n \cdot {}^{\ominus}G_{\mathrm{C}}^{\mathrm{gr}})$ in equation (12) can be taken as the Gibbs mole formation free energy of two kinds of substances. The former is given by the experiment of M. Hillert[5], the latter can be calculated from general thermodynamic data[6]. The thermodynamic data from calculation of carbon activity are listed in table 2. As to $L_{\mathrm{cv}}^{\mathrm{MC}}$, because VC layer has the same fcc structure as austenite substrate, $m=n=1$, both have the same reactive energy between carbon atom and vacancy on cavity sub-lattice of fcc structure. Set $L_{\mathrm{cv}}^{\mathrm{VC}} = L_{\mathrm{cv}}^{\mathrm{A}}$, according to Uhrenius's method[7], values of activity calculated from eqations (11) and (12) on basis of data in table 2 are listed in table 1. The carbon activity in the substrate becomes smaller with higher temperature while the carbon activity in the layer becomes bigger with higher temperature.

Table 2 Thermodynamic data for activity calculation

J/mol

${}^{\ominus}G_{\mathrm{FeC}}^{\mathrm{A}} - {}^{\ominus}G_{\mathrm{Fe}}^{\mathrm{A}} - {}^{\ominus}G_{\mathrm{C}}^{\mathrm{gr}}$	67 194−70 623 T
${}^{\ominus}G_{\mathrm{VC}}^{\mathrm{VC}} - {}^{\ominus}G_{\mathrm{V}}^{\alpha} - {}^{\ominus}G_{\mathrm{C}}^{\mathrm{gr}}$	−102 100+9 058 T
${}^{\ominus}G_{\mathrm{V}}^{\alpha} - {}^{\ominus}G_{\mathrm{V}}^{\gamma}$	−9 000−3.56 T
$L_{\mathrm{CV}}^{\mathrm{A}}$	−21 097−11.555 T
J_{Si}	10 000
J_{Mn}	−41 000
J_{Cr}	−251 100+118 T
J_{Mo}	−100 000
J_{V}	−180 000

The diffusion coefficient D_{C} of carbon in VC layer is determined by regression of the experimental data. In general, the alloy elements in steel substrate except carbon and nitrogen don't diffuse towards the layer, so the carbide layers formed on surface of different kinds of steels have the same composition, structure and the value of D_{C}. The values of D_{C} regressed from the experimental results according to equation(6) have good consistency ($5.89 \times 10^{-11} \sim 5.93 \times 10^{-11}$ cm^2/s) for 45 and T10 steels containing lower alloy and high alloy steel 4Cr5MoSiV1 and Cr12MoV at the temperature above 1 000℃. This shows the excellent adaptability of equation (6).

Substitute values of $a_{\mathrm{C}}^{\mathrm{A}}$, $a_{\mathrm{C}}^{\mathrm{F}}$ and D_{C} obtained above into equation (6), the relationships between thickness of VC layer, time, temperature and activity are illustrated as line segments in Fig. 1, Fig. 2 and Fig. 4. The points in the plot are the experimental results measured. By comparison of the calculated results with the experimental results, the kinetics equation of growth of carbide layer set up had ideal consistency with the experimental results.

As shown in Fig. 1, the calculated and measured results showed that the thickness of the layer has a nearly parabolic relation with treatment temperature. Increasing treatment temperature can improve the growth speed of VC layer. According to alloy thermodynamics, the carbon activity of high alloy steel calculated from the model of regular solution sub-lattice is higher than that of real steel for such middle-high alloy steel as 4Cr5MoSiV1 and Cr12MoV at the temperature below 1 000℃, therefore, the calculated value of the thickness of layer is a little higher than the value measured as shown in Fig. 1.

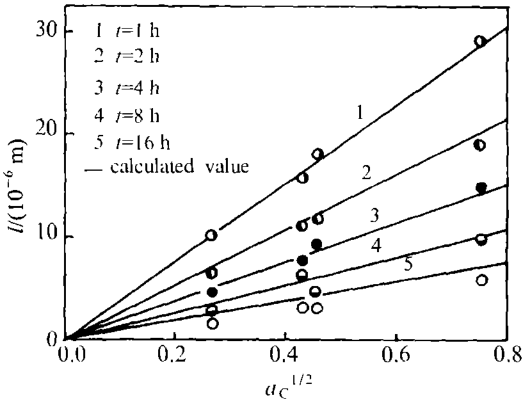

Fig.4 Relation between layer thickness and carbon activity in substrate (1 000℃)

The experimental data in Fig. 2 and calculated results from eqations (11) and (12) showed that, for steel 4Cr5MoSiV1 and Cr12MoV, though the carbon content of the former is near to steel 45, the latter is far higher than steel T10, due to high content of strong CFE, the carbon activity is reduced, the diffusion driving force is cut down largely, and the growth speed of carbide layer on the surface is slowed down.

From equation (7), it was known that when the carbon activity in VC layer is small, the thickness of layer is nearly proportional to the square root of carbon activity in substrate, this relation was testified well by the experimental results shown in Fig. 4. Different carbides have different range of carbon content, therefore, from relation (7), the carbide layers with wide range of carbon content such as TiC(x_C=18~50) and ZrC(x_C=21~50) etc. should have higher speed if the diffusion coefficients are the same.

4 Conclusions

(1) The growth speed of the carbide layer formed on surface of steel is mainly controlled by treatment temperature and carbon activity in the substrate. Under experimental condition, the thickness of layer is nearly in linear relation with the square of treatment temperature and square root of the carbide activity in the substrate.

(2) The kinetics equations of growth of carbide layer on the surface of steel proposed in this paper can be applied to calculating the thickness of layer, because the results calculated from this equation has good agreement with the experimental results.

(3) When calculating the carbon activity of middle-high alloy steel using this model of regular solution sub-lattice, more consideration should be given to the solubility of the carbide in the steel below 1000℃ .

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