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Thermodynamic analysis of carbon migration in W1-1.0C steel in plasma surface chromizing

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Abstract: W1-1.0C steel was chromized at 1173 K with double glow plasma surface alloying process, and the distribution of Fe, Cr, and C contents in the chromized layer was measured using glow discharge spectrum analysis (GDA). The behavior and mechanism of carbon migration during the formation of chromized layer were studied through thermodynamic analysis and calculation. The gradient of carbon chemical potential was regarded as the driving force of carbon migration. An equation was derived to describe the carbon content varying with the chromium content within the carbon-rich region. The calculated results from the equation approximated closely to the experimental ones.

Key words: carbon steel; chromizing; thermodynamic analysis; surface alloying; carbon migration

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1. Introduction

A high hardness alloyed layer was formed on the surface of carbon steel after chromizing, which improved its surface property significantly [1-4]. The addition of chromium turned the binary system Fe-C, Fe-Cr-C ternary system at the surface alloyed region where the chromium content changed gradually from the surface toward the inner part. The carbon distribution in the austenite was also disturbed, a carbon-rich zone occurred at the chromized layer and the distribution of C was changed in the austenite, which resulted in a high carbon content called carbon-rich region in the chromized layer whilst a carbon depleted zone was formed in the adjacent substrate material [5]. The phenomena indicated that carbon migration happened as a result of the interaction between chromium and carbon during the alloying process, which would affect the microstructure and properties of the substrate material. In this study, thermodynamic calculation of Fe-Cr-C ternary system was conducted to analyze the carbon distribution in the chromized layer and the mechanism behind the carbon re-distribution.

2. Experiment

Fully annealed commercial W1-1.0C steel was selected as the experimental material. Samples with dimensions of 30 mm×20 mm×5 mm were cut and polished, then cleaned and degreased. The chromizing processes were carried out at 1173 K for 1, 2, 3 h respectively with the double glow plasma surface alloying technique [3-6] and then cooled to room temperature rapidly. The processing parameters were as follows: the distance between sputtering target and substrate, 20 mm; sputtering voltage, 800 V; discharge gas pressure, 45 Pa (argon); substrate bias, 280-350 V. The Fe, Cr, C content profiles in chromized layers were measured with GDA750 glow discharge spectrum analyser (GDA, Spectro A.I., Germany).

3. Results and discussion

3.1. Carbon migration of W1-1.0C steel

Figs. 1-3 are the microstructures of chromized layers. The corresponding composition (wt%) distributions are shown in Figs. 4-6 respectively.

From the composition distribution results, the carbon migration exists at chromizing time and the peak value of carbon content in the carbon-rich zone appears in the high chromium content region. The carbon peak occurs in the sample chromized for 1 h at 0.1 μm from the surface, the width of the peak is about 9.0 μm and the peak value is 6.9%, while in the carbon-depleted region the minimum carbon content is only 0.54%; at 2

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h, the peak value 7.8% is located at 4.5 μm from the surface and the width is 12.5 μm, the minimum value in the carbon depleted region is 0.55%; at 3 h, the carbon peak shifted to 5 μm from the surface, the width enlarges to 15 μm and the value is around 7.2%, and the corresponding minimum carbon content in the carbon-depleted region is only 0.59%.

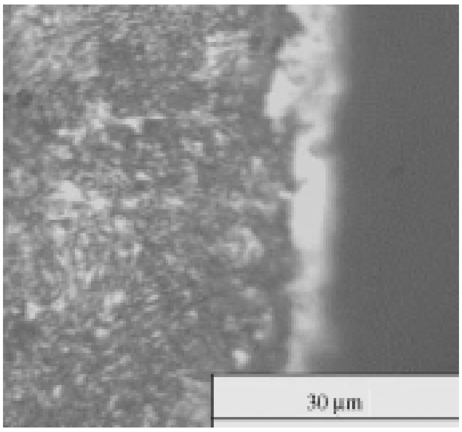

Fig. 1. Microstructure of the chromized layer of W1-1.0C steel sample (1 h).

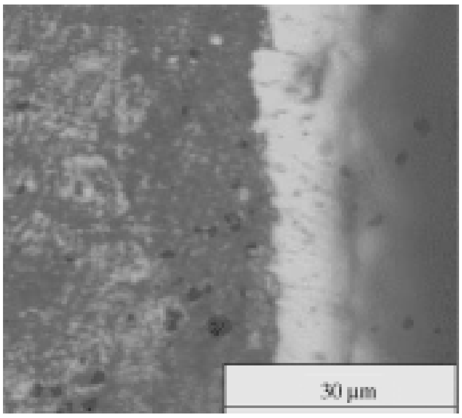

Fig. 2. Microstructure of the chromized layer of W1-1.0C steel sample (2 h).

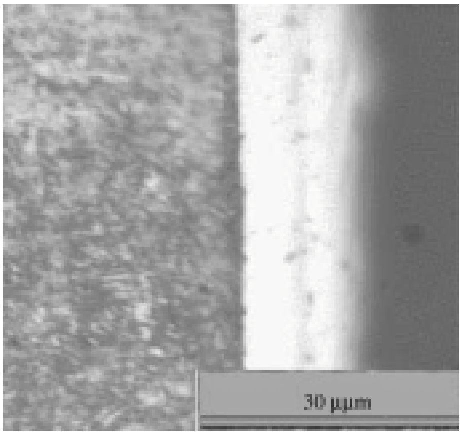

Fig. 3. Microstructure of the chromized layer of W1-1.0C steel sample (3 h).

It is obvious that with the increase of chromizing time, the width of the carbon-rich region increases, the carbon content peak shifts inward and the value remains at 6.9%-7.8%; the minimum carbon content in the carbon-depleted region is lower than 60% of the original content.

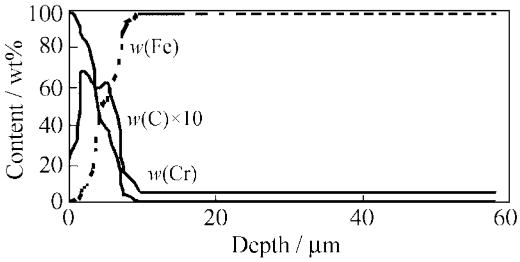

Fig. 4. Profiles of element distribution in the surface layer of W1-1.0C steel sample (1 h).

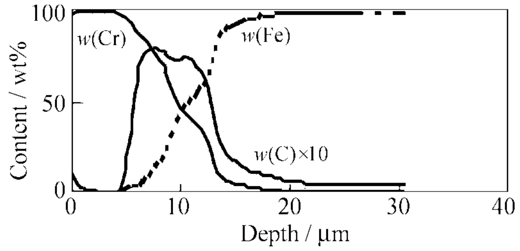

Fig. 5. Profiles of element distribution in the surface layer of W1-1.0C steel sample (2 h).

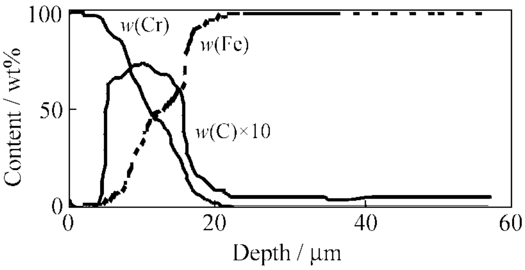

Fig. 6. Profiles of element distribution in the surface layer of W1-1.0C steel sample (3 h).

3.2. Carbon activity of Fe-Cr-C austenite

At a chromizing temperature of 1173 K, carbon in the substrate Fe-C binary alloy dissolves in austenite as interstitial atoms while the Fe atoms stay at the lattice points. As chromium diffuses into the surface layer, the Fe-Cr-C ternary system with gradient chromium content is formed, while the emerging chromium atoms dissolve in austenite as substitutional atoms, which occupy the positions of Fe atoms at the lattice. As a result, the austenite of the ternary system takes the form of solid solution with both substitutional and interstitial characters.

Based on the fact that Fe atoms take the positions of lattice points and C atoms of lattice gaps, Chipman assumed that the amount of interstitial sites equals that of Fe atoms in γ-Fe and drew the conclusion that carbon activity in the Fe-C austenite is directly proportional to the ratio of the amount of interstitial sites filled by C atoms to that not filled by C atoms. Furthermore, through carburizing experiments on Fe-Cr alloys with different chromium contents and by analyzing the Fe-C austenite, he proposed the expression of carbon activity in the Fe-Cr-C ternary austenite [8]:

$$\alpha_C = f_C * w(\mathrm{C}) \tag{1}$$

$$\lg f_C = 2300/T - 2.24 + (179/T) * w(\mathrm{C}) + (0.033 - 102/T) * w(\mathrm{Cr}) \tag{2}$$

where α_C is the carbon activity (graphite as the standard state); f_C the carbon activity coefficient (graphite as the standard state); T the austenite temperature, *i.e.* chromizing temperature, K; w(Cr) and w(C) are the chromium and carbon mass fraction respectively.

From Eqs. (1) and (2), we can work out the carbon activity in W1-1.0C steel at 1173 K with different chromium contents as shown in Table 1. It is clear that carbon activity reduces dramatically with the increase of chromium content, which proves that chromium significantly affects the carbon activity in austenite.

3.3. Carbon chemical potential in the Fe-Cr-C austenite

At a certain temperature, carbon chemical potential μ_c and the logarithm of carbon activity in the Fe-Cr-C austenite are in the relationship of linear increasing function [9]:

$$\mu_c = \mu_c^* + RT \ln \alpha_c \tag{3}$$

where μ_c^* is the graphite chemical potential in standard state; R the gas constant; T the austenite temperature, *i.e.* the chromizing temperature, K.

Table 1. Activity of carbon in W1-1.0C steels with different chromium contents at 1173 K

w(Cr)	0	5	10	15	20
$\lg f_C$	–0.1266	–0.3964	–0.6661	–0.9359	–1.2055
α_C	0.7471	0.4014	0.2157	0.1159	0.0623

Table 1 and Eq. (3) show that the diffusion of chromium causes the decrease of carbon activity in the chromized layer, and also causes the decrease of carbon chemical potential in the austenite. Therefore, the gradual descending chromium content from the surface leads to the gradual change of carbon chemical potential in the opposite direction, in other words, decreases from the substrate austenite to the surface. Carbon chemical potential is the carbon's capability to escape from austenite, and it always moves from the phase with higher chemical potential to the phase with lower chemical potential. This explains the uphill diffusion of carbon from substrate to the chromized layer and the formation of the carbon content peak within the alloyed layer, where the driving force is the gradient of chemical potential, not the concentration gradient.

3.4. Carbon content in the chromized layer

Fig. 7 shows that chromium carbide phases, such as (Cr, Fe)$_{23}$C$_6$, (Cr, Fe)$_7$C$_3$ *etc*., are formed as chromium diffuses into carbon steel surface. In the above three types of chromium carbide, the carbon content in (Cr, Fe)$_7$C$_3$ is the highest. During the chromizing process, if Fe atoms are completely substituted by Cr atoms, the carbon content in the chromized layer will be the maximum. The following Eq. helps to estimate the highest carbon content:

$$w(\mathrm{C}) = \frac{12 \times 3}{12 \times 3 + 52 \times 7} = 9\%.$$

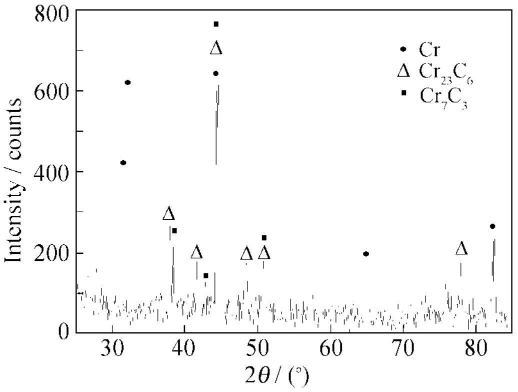

Fig. 7. XRD pattern of W1-1.0C sample.

Actually, all the three types of chromium carbide co-exist in the Fe-Cr-C system of the surface chromized layer, and each contains certain amount of Fe. Therefore, the real carbon content would not exceed 9% as calculated above. The experimental results in Figs. 4-6 show that the carbon content peak falls in a range of 6.9% to 7.8%.

During the chromizing process at a certain temperature, with the increase of Cr content, to keep its original carbon activity unchanged, the austenite substrate must continuously increase its carbon content. Therefore, the relationship between carbon content and chromium content in the chromized layer at 1173 K could be obtained.

From Eq. (2), the logarithm of carbon activity coefficient in the Fe-C austenite before chromizing is:

$$\lg f_{\mathrm{C}}^{'} = \frac{2300}{1173} - 2.24 + \frac{179}{1173} \times 1.0 = -0.1266 \tag{4}$$

While chromizing, there exists the following relationship between the logarithm of carbon activity coefficient in the Fe-Cr-C austenite and Cr, C content:

$$\lg f_{\mathrm{C}}^{''} = \frac{2300}{1173} - 2.24 + \frac{179 \times w(\mathrm{C})}{1173} + \left(0.033 - \frac{102}{1173}\right) \times w(\mathrm{Cr}) = -0.2792 + 0.1526 w(\mathrm{C}) - 0.05396 w(\mathrm{Cr}) \tag{5}$$

If the carbon content before and after chromizing in the austenite is the same, then:

$$\alpha_{\mathrm{C}}^{'} = \alpha_{\mathrm{C}}^{''} \tag{6}$$

Put Eqs. (4) and (5) into Eq. (6):

$$\lg\left(\frac{w(\mathrm{C})}{1.0}\right) = 0.1526(1.0 - w(\mathrm{C})) + 0.0540 w(\mathrm{Cr}) \tag{7}$$

Eq. (7) is the relationship between carbon content and chromium content during the chromium diffusion in W1-1.0C steel which could describe the carbon migration as the chromized layer is formed. According to the equation, the calculated carbon content conforms well with the experiment results in Figs. 4-6, where the chromium content is less than 20%.

4. Conclusions

(1) When chromized with double glow plasma surface alloying process, the chromium diffusion in W1-1.0C steel causes the decrease of carbon activity in the chromized layer and the decrease of carbon chemical potential as well. The descending chromium content distribution from the surface leads to the gradual decrease of carbon chemical potential in the austenite from substrate to surface and results in uphill diffusion of carbon from substrate to surface. The driving force of carbon migration is the gradient of carbon chemical potential, rather than the gradient of carbon content.

(2) Carbon migration runs continuously during the whole process of chromizing and carbon-rich region is formed in the surface layer. Carbon content peak value appears in high chromium content region, and carbon-depleted region is formed in the subsurface layer.

(3) With the increase of chromizing time, the width of the carbon-rich region in W1-1.0C steel increases, carbon content peak shifts inward, and the peak value stays between 6.9% and 7.8%. The minimum carbon content in the carbon-depleted region is less than 60% of the original carbon content in the substrate.

(4) According to the criterion that the carbon activity before and after chromizing in the austenite remains the same, the relationship between carbon and chromium content is derived as:

$$\lg\left(\frac{w(\mathrm{C})}{1.0}\right) = 0.1526(1.0 - w(\mathrm{C})) + 0.0540 w(\mathrm{Cr}).$$

The calculating result conforms well with the experimental result.

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