Precipitation Behavior on Carbon Steel Modified by Double Glow Plasma Surface Alloying with W and Mo

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Many brittle precipitates appeared in the alloyed layers which were formed in surface modified carbon steel by DGPAS (Double Glow Plasma Surface Alloying) with W and Mo because of the slow cooling rate in the alloying furnace. As a result, the mechanical properties of these alloys were significantly degraded by precipitation of the brittle phase. Phase analysis of the electro-extracted precipitates by X-ray diffraction (XRD) revealed that they were mainly composed of the μ-phase and a small amount of carbide, M₆C. In the present study, their microstructures were characterized by optical microscopy (OM) and scanning electron microscopy (SEM). It was concluded that the chemical components, temperature and time were the main thermodynamic factors influencing their deposition. The isothermal transformation (IT) diagram of the precipitates showed that there were two transforming climaxes. Based on the IT diagram, a technique was developed to depress the precipitate deposition.

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Keywords: thermodynamics, phase transformation, precipitates, isothermal transformation diagram

1. Introduction

Double Glow Plasma Surface Alloying technology (DGPAS) is a valuable surface metallurgical technique, which is used to form an alloying layer on the surface of a conductor. This method is heavily based on the theory of glow discharge. DGPAS with the elements of W–Mo–C can improve the abrasion resistance of materials and lengthen their service life, which has already been applied to saw blades. However, saw blades sometimes break along their tooth roots when they were tested. Su and Wang indicated that this was due to the slow cooling rate after the DGPAS process with W and Mo during which the precipitates were formed in the alloyed layers. They always precipitated along the grain boundaries. To depress the precipitate formation and improve the saw blade’s mechanical property, the precipitation behavior in the surface modified layer was investigated in this study.

2. Experimental

2.1 Materials

The substrate material used in the present investigation was carbon steel Fe–0.2C (mass%). Test samples were prepared from commercial saw blades composed of this steel and cut into 100 mm × 10 mm × 0.8 mm specimens.

2.2 Alloying by DGPAS with W and Mo

Figure 1 shows a schematic diagram of the setup for this process. The cathode was first turned on to heat and clean the specimen by radiation from the heater elements in the chamber that was filled with low-pressure argon. Second, the source electrode was supplied with power when the specimen temperature approached 1473 K which was determined by a photocell pyrometer. Simultaneously, glow discharge occurred at two places: one was between the anode and the cathode, the other was between the anode and the source electrode. This is why the technology was called double glow plasma. The source electrode was an alloy plate made from 50 W and 50 Mo (mass%), which was sputtered by ionized argon and produced a specimen with activated W and Mo. An alloyed layer containing W and Mo was finally formed. The alloying time and temperature as well as the power imposed on the electrode influenced the layer thickness. Some experimental parameters are listed in Table 1.

![Fig. 1 The schematic diagram of set-up for the technology of DGPAS.](image)

<table>
<thead>
<tr>
<th>Table 1 Some experimental parameters of DGPAS.</th>
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<tr>
<td>Working pressure</td>
</tr>
<tr>
<td>20–30 Pa</td>
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</table>

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2.3 IT diagram determination of the precipitates

The samples were heated according to the given technological conditions in the Embedded Salt-bath Resistor furnace immediately after the redissolution at 1533 K for 360 s, then quenched in water. A quantitative metallographic automatic image analyzer was used to determine the IT diagram in accordance with the theory of stereoscopic and quantitative metallography. To attain the transformation fraction of the precipitates under a certain condition, six different viewing fields were selected randomly in the same specimen, then each $A_\Lambda$ (the area fraction of precipitates) was measured and the average value was calculated as the final experimental data plotted in Fig. 2. In the present study, its data measuring accuracy was 4%, and the degree of confidence was 95%.

The precipitates were electro-extracted by a constant current in a mixture of hydrochloric acid, citric acid and methanol in the temperature range from 263 K to 268 K. X-ray diffraction (XRD) using Cu Ka radiation, optical microscope (OM) and scanning electron microscopy (SEM) were used to study the microstructure and the morphologies of the precipitates.

3. Results and Discussion

3.1 Microstructure of the precipitates

Figure 3 shows the cross-section optical morphology of the precipitates formed along the grain boundaries as well as in the grains that were deposited during the slow cooling period in the DGPSA furnace after alloying with W and Mo. However, they completely disappear after redissolved at 1533 K for 360 s.

Figures 4(a) and (b) show the back-scattering-electron cross-section images of the precipitates at 1173 K for 1200 s and 1223 K for 720 s, respectively, which are mainly in the thin stick-like and needle-like form in the grain or along the grain boundaries. Figure 4(c) shows the images at 1373 K for 2400 s, which are in a coarse irregular block-like form. As a side note, the round phase in Fig. 3 and Fig. 4 are new to us and will be discussed in a future paper.

Figure 5 shows the X-ray diffraction spectra for sample 1 and sample 2. Sample 1 was alloyed at 1223 K for 6000 s and sample 2 was alloyed at 1423 K for 6000 s. The peaks in sample 2 are identified as the $\mu$-phase, which molecular formula was Fe$_7$(W, Mo)$_6$. Some extra peaks appear in sample 1, which originate from the carbide, $\mu_\Lambda$C, that exhibits one of the differences in the precipitates at the various temperatures. Thus, the precipitates are mainly composed of the $\mu$-phase, which is a kind of top compacted phase (TCP) and negatively affect the mechanical properties of the specimen, especially, when it is deposited along the grain boundaries.

3.2 IT diagram of the precipitates

Because of the variation in the W and Mo contents at the different depths in the alloyed layer, the 100 $\mu$m depth was chosen as the standard depth for this study. The total thickness of the alloying layer was generally about 600 $\mu$m. Based on the EDX results, the scattering of the contents is shown in Table 2 and Table 3. The carbon and impurities in the steel are not concluded. Because serious decarburization occurred in the alloying process, the carbon content in the alloyed specimen was far less than that of the original ones which is 0.2 mass%. The average value after alloying was 0.03 mass%, which was measured by nonaqueous titration. There was no doubt that their uniformity was essential for this research. Therefore, several actions were taken to decrease the scattering. Although the results are satisfactory, further research is needed.

We measured the isotherms of the precipitates (see Fig. 2). The 5% transforming curve is considered as the starting line, and at the meantime, the 20% transforming curve is given. In Fig. 2 two data points denoted by "o" were extrapolated by LaGrange's method as follows:

$$
y = y_1 \left[ \frac{x - x_2}{x_1 - x_2} \times \frac{x - x_3}{x_1 - x_3} \times \frac{x - x_4}{x_1 - x_4} \times \ldots \right] + y_2 \left[ \frac{x - x_1}{x_2 - x_1} \times \frac{x - x_3}{x_2 - x_3} \times \frac{x - x_4}{x_2 - x_4} \times \ldots \right] + \ldots \quad (1)
$$

Where $x_1 \sim x_i$ and $y_1 \sim y_i$ refer to the alloying time and transformation fraction of the experimental data at the two temperatures, 1323 K and 1223 K, respectively.
The IT diagram has two distinguished features. (1) Due to the carbide (M₆C) formation in the lower temperature and the different μ-phases (Fe₇(W,Mo)) formed in the tested temperature range, two transforming climaxes appear. One “nose temperature” is 1423 K and the incubation period is 360–480 s; the others are 1223 K and 240–300 s (see Fig. 2). The molecular formula of μ-phase was Fe₇(W,Mo). The contents of W and Mo are different from each other at the different temperature stages. (2) The isotherm is shaped “C”, which is typical for the diffusing phase transformation. The different incubation period occurred in the different temperatures, during which the phase transformation was prepared. However, some argued that the transformation has begun in the period. As far as the author concerned, it is mainly the preparation stage for the transformation. When the concentration of the alloying elements, W and Mo, reaches a critical value, the transformation will begin. However, it seems to be impossible to determine the exact point, so the researchers often stipulate the starting point in the light of the study itself.

3.3 Thermodynamics factors influencing the formation of the μ-phase

When the samples were alloyed at 1473 K, the microstructure was austenite. It is well known that W and Mo are both ferrite former elements. Their diffusion into the samples will enlarge the area of α phase and reduce that of γ phase. When their concentration reached a critical value, a phase transformation, γ → α, occurred. As the alloying process went on, an alloyed layer, i.e., the α solid solution was built up on the surface of the samples. During the cooling period after alloying the solubility of W and Mo in the α solid solution decreased. As a result, a new phase was deposited in the layer. Moreover, different morphologies formed under different conditions.

The former process of the μ-phase is a typical diffusion transformation. The nucleation and its growth largely rely on the thermal activation. Therefore, the factors that affect the μ-phase transformation are also those that have effects on its nucleation and grain growth.

The first factor is the chemical composition. Woodyatt et al. found that the mean electron density number was very important for the μ-phase formation, which is calculated from
Table 4 The chemical factors for the formation of $\mu$-phase.

<table>
<thead>
<tr>
<th>Sample NO.</th>
<th>(W + Mo) (mass%)</th>
<th>[Mo/(W + Mo)] (at%)</th>
<th>$N_v$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>7.70</td>
<td>69</td>
<td>2.74</td>
</tr>
<tr>
<td>2</td>
<td>6.74</td>
<td>72</td>
<td>2.74</td>
</tr>
<tr>
<td>3</td>
<td>7.37</td>
<td>70</td>
<td>2.74</td>
</tr>
<tr>
<td>4</td>
<td>7.77</td>
<td>75</td>
<td>2.74</td>
</tr>
<tr>
<td>5</td>
<td>5.66</td>
<td>75</td>
<td>2.72</td>
</tr>
<tr>
<td>6</td>
<td>7.71</td>
<td>81</td>
<td>2.74</td>
</tr>
<tr>
<td>mean</td>
<td>7.16</td>
<td>74</td>
<td>2.74</td>
</tr>
</tbody>
</table>

The following equation:

$$\tilde{N}_v = \sum_{i}^{n} m_i (N_v)_i$$  \hspace{1cm} (2)

where: $\tilde{N}_v$ is average electron vacancy number, $m_i$ is the atomic fraction of particular element in the alloyed layer, $N_v$ is individual electron vacancy number of particular element and $n$ is number of elements of the alloyed layers.

It was concluded that the value of the critical number of alloy electron vacancy was 2.30. In other words, any alloy, which has an $N_v$ value larger than 2.30, is considered suspect for the $\mu$-phase transformation. Cai Yulin et al.\(^7\) indicated that in addition to $N_v$ value, the following two parameters, (W + Mo) mass% and [Mo/(W + Mo)] at%, were also critical. Generally, when the value of (W + Mo) mass% is higher than 10%, the $\mu$-phase transformation will occur. Table 4 shows our experimental results for these parameters, which originated from the data in Table 3. The average value of $N_v$ is 2.74, that of [W + Mo] mass% is 7.16% and that of [Mo/(W + Mo)] at% is 74%. It can be concluded that the values of $N_v$ and [Mo/(W + Mo)] at% are the main factors of the $\mu$-phase formation in the present study.

The second factor is temperature. Many of $\mu$-phase formed after the samples were cooled in the DGPSA furnace. In order to redissolve the precipitated $\mu$-phase into the substrate, the samples were put into the tube furnace at 1533 K for 360 s. Immediately thereafter, they were heated at the different temperatures to deposit the $\mu$-phase again. The difference between the two temperatures is called super cooling that is directly related to the $\mu$-phase nucleation and its grain growth. When it increases, the critical radius of the nucleus and the energy for nucleation are both decreased, and it is easier to form a stable nucleus.

The third factor is time. Its influences are shown by the following two aspects. One is its incubation period, i.e., the transportation time of the alloying elements, W and Mo. The other is that the nucleus will grow larger along with the increase of soaking time. Besides the factors discussed above, there are still other elements that affect formation of the $\mu$-phase. For example, the original grain size of the $\alpha$ phase and the crystal defects. When the alloyed samples are heated at the high temperatures for a long time, the amount of grain boundaries, which serves as helpful nucleation sites, is reduced. Therefore, the possibility of nucleation in the grains will be increased.

3.4 Effective method to depress the precipitate deposition

The content of alloying element can be reduced as possible, so long as the technical condition can be satisfied. It may be achieved by lowering the alloying temperature or shortening the alloying time. However, lowering temperature means prolonging the alloying time, while shortening the alloying time means having higher alloying temperature. How does one then control its formation? Changing the content of the source electrode is thought to be a good method. However, under the present technological conditions, an effective method is to raise the cooling rate after alloying at 1473 K in order to limit its incubation.

Taking into account the influence of cooling process on the equipment and specimens, the cooling technology is determined from the IT diagram as follows: specimens are cooled from 1473 K at the rate of 1 K/s for 360 s, then gradually cooled. Such a condition is easy to obtain in practice and its effect upon the equipment and the work pieces can be neglected.

4. Conclusions

1) The qualitative determination of the precipitates in surface alloying later on carbon steel by DGPSA with W and Mo showed that they were mainly composed of the $\mu$-phase and a small amount of carbide, $\text{M}_6\text{C}$. As for the morphology of the precipitates, there were two kinds, one was thin needle-like and the other was thick block-like.

2) The isothermal transformation of the precipitates was the typical diffusing phase type. There were incubation periods at different isothermal stages. Due to the influence of temperature on the precipitates, the incubation period reached the plateau and the entire curve was “C” shaped. The quickest transforming rate occurred at 1423 K and 1223 K, and their incubation periods were 360–480 s and 240–300 s, respectively.

3) In addition to the alloying temperature and time, the values of $N_v$ and [Mo/(W + Mo)] at% were important factors that influenced the $\mu$-phase formation.

4) As the main application of this project, we calculated the optimal cooling condition on the basis of the IT diagram in order to control the $\mu$-phase formation. It was cooled from 1473 K at the rate of 1 K/s for 360 s, then the rate was slowed down in order to protect the equipment and specimens.

REFERENCES