Effect of vacuum carburizing on surface properties and microstructure of a tungsten heavy alloy

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Keywords: vacuum carburizing, tungsten heavy alloy, WC, depth of infiltration layer

Abstract
Vacuum carburizing of the R2M tungsten alloy was carried out to obtain a carburized layer that improves the surface properties. The effects of various carburizing temperatures and times on the structure and hardness were studied by Optical microscopy (OM), x-ray Diffraction (XRD) and Scanning electron microscope (SEM). In this work, the microstructure of the carburized layer, the relative content of the surface layer, the depth of the layer and the microhardness of the carburized sample were studied. The results show that the microstructure exhibited three layers from the surface to the bulk of the sample after carburizing. The outside layer comprised a 40 ~ 60 μm deep WC carburized layer. The hardness of the surface layer (396 HV) was significantly higher than that of the substrate (282 HV). As the carburizing temperature and time increased, the WC and W content of the surface layer of the sample gradually increased, and the depth of the carburized outer layer increased.

1. Introduction
Die-casting molds are used in poor service conditions, leading not only to stringent requirements for the mechanical properties of the mold materials, but also to high requirements for wear resistance, corrosion resistance and surface properties [1]. Unfortunately, several commonly used kinds of die steels, such as H13, H11 and 4Cr4Mo3V, are prone to deformation and surface microcracks due to mechanical stress and thermal stress experienced in actual use. In addition, their fatigue resistance is poor and the service life of the mold is short [2]. Therefore, many researchers have attempted to use high melting point refractory ferrous metals, such as molybdenum-based alloys or tungsten-based alloys, to make a die-casting mold to replace the traditional mold steel material. Among these, high-density R2M tungsten alloy has a high melting point, high density, good thermal conductivity and low coefficient of linear expansion, and is an ideal material for die-casting molds [3–5].

In previous studies, the study of tungsten alloys has focused on the addition of alloying elements [6, 7], grain refinement [8–11] and plastic deformation [12–14]. However, there have been relatively few studies on the surface modification of tungsten alloys. For a die-casting mold material, the wear between the contact surfaces and the surface coating peeling off when the mold is opened and closed will destroy the surface integrity of the mold, greatly affecting the performance and lifetime of the mold. Therefore, research on the surface modification of R2M tungsten alloy is also extremely important. Carburizing is a commonly used surface modification method in mechanical manufacturing [15]. This process has traditionally been applied to steel materials, but in recent years it has been extended to materials such as titanium alloys and tungsten alloys. Xu et al [16] explored the optimal carburizing heat treatment process for surface-lean Co-free η phase WC-Co cemented carbide, which provided an important reference value for the carburizing heat treatment of the alloy. Eroglu et al [17] introduced the C element into the 92 W surface layer by plasma to enhance its wear resistance. Hu et al [18] carburized 95 W, forming a new carburized layer on the surface layer, and found that the inner layer consists of shell-like carbide wrapped W particles, and the outer layer is a porous WC polymer. To date, there have been few reports on the surface treatment of the R2M tungsten alloy by the vacuum carburizing technique.
The influence of the specific process parameters on the depth of the carburized layer and the carburizing product remains to be explored.

In this work, the surface treatment of the R2M tungsten alloy is carried out by the vacuum carburizing process, and the goal of strengthening the surface of the material is achieved using the carbonized layer. The effects of the carburizing temperature and carburizing time on the carburizing effect of the R2M tungsten alloy were studied from the microstructure of carburized layer, the relative content of the surface layer, the depth of the infiltration layer and the microhardness, in order to determine the characteristics of the R2M tungsten alloy. The optimal carburizing parameter provides a reference for the surface strengthening method of the R2M tungsten alloy.

2. Materials and methods

The chemical composition (wt%) of the high-density R2M tungsten alloy is listed in table 1. A tungsten heavy alloy (R2M) sintered by powder metallurgy was selected for this study. Its tensile strength and yield strength at room temperature were 990 MPa and 750 MPa, respectively. Figure 1 shows the original microstructure of the R2M tungsten alloy. The grey equiaxed grains indicate the matrix, which mostly consists of tungsten, and the remaining black areas is the $\gamma$-(Ni, Fe) phase.

The original sample was processed into a cylindrical sample with a size of $\Phi 8 \times 6$ mm using a numerically controlled wire cutting machine, and the surface of the sample was polished by water sandpaper, followed by vacuum carburization. The carburizing treatment was carried out using a WZSJ-200 two-chamber vacuum carburizing furnace. The ratio of carburizing time and diffusion time was set to 1:2. The carburizing temperatures and times are shown in table 2. The microstructure of the specimens was examined by OM with an Olympus BH2 instrument. X-ray diffraction (XRD, Bruker D8-ADVANCE) with Cu $k_\alpha$ radiation, a scan angle ($2\theta$) of 0°~120° and voltage 28.0 kV was employed to determine the crystallographic phases in the untreated and carburized specimens. Microstructure observations were performed using a SUPRA 40 (ZEISS) type scanning electron microscope with the voltage 10.0 kV. The surface gradient hardness test of the axial section of
the carburized sample was carried out using a HVS-1000 Vickers microhardness tester with a load of 4.9 N, and measurements were repeated every 50 \( \mu m \) for a total distance of 400 \( \mu m \) from the carburized surface. The measurements were carried out three times, and averaged. Then, measurements were taken every 100 \( \mu m \) until the total distance of 2.2 mm was reached.

### 3. Results and discussion

#### 3.1. Effect of carburization on the microstructure

Figure 2 shows the original microstructure of the R2M high-density tungsten alloy and the metallurgical structure of the tungsten alloy after vacuum carburizing at 950 °C, 900 °C, and 850 °C for 180 min. Figure 2(a) shows the original metallographic structure of a typical R2M tungsten alloy. The W particles are uniformly distributed in the structure as spherical particles, and the \( \gamma \) phase (JCPDS file No26-0790) acts as a binder phase \[19\]. It can be seen from figures 2(b)–(d) that after the carburizing treatment, a sharp black carburized layer appears in the surface layer of the R2M sample, and in the carburized layer region, the W particles have non-rounded corners. The black carburized particles are attached to the periphery, indicating that the C element diffuses into the tungsten alloy during the carburizing process, and the core structure hardly changes and is consistent with the original structure. Moreover, the carburized layer on the surface of the sample after vacuum carburizing at 950 °C is deeper than that after carburizing at 900 °C and 850 °C, the black carbonized layer on the surface is thicker, and a higher degree of carbonization is obtained for locations closer to the surface layer. From a thermodynamic point of view, the reaction temperature is increased and the diffusion coefficient is effectively increased. The increase in the carburization temperature increases the activity of the C atoms, so the C atoms migrate easily, and react to an increased extent with the matrix; On the other hand, as the carburization temperature increases, the amount of the R2M tungsten defects, such as vacancies in the alloy, increase accordingly, resulting in an increase in the diffusion rate of the C atoms in the W matrix and an increase in the rate of formation of the carburized layer. Therefore, the surface carburization layer of the sample is more pronounced at 950 °C than at the other temperatures considered in this study.

Figure 3 shows the original structure of the R2M high-density tungsten alloy and the microstructure of the sample after vacuum carburizing at 950 °C for 180, 120, and 60 min. It is observed from the figures that when the carburizing temperature is constant, there is a difference in the metallographic structure of the sample for different carburizing times. The depth of the carburized layer after 180 min is greater than that of the sample.
with carburizing times of 120 min and 60 min. This shows that as the carburizing time increases, the depth of the carburized layer gradually increases.

### 3.2. Influence of carburization on the phase

Figure 4(a) shows the original surface of the R2M tungsten alloy without carburization and the surface XRD diffraction analysis of the sample after carburizing at 950 °C, 900 °C, and 850 °C for 180 min. As observed from figure 4(a), the original R2M tungsten alloy mainly consists of a W phase matrix phase and a γ phase. After carburizing, in addition to the diffraction peaks of the W phase and the γ phase of the matrix phase, a large number of phase diffraction peaks appear, indicating that C atoms diffuse into the R2M tungsten alloy matrix during the carburizing process and chemically react with the W element in the alloy. As a result, carbides are formed. The diffraction peak intensity of the W matrix phase and the diffraction peak intensity of the WC(JCPDS file No.51–0939) are both high, indicating that the black carburized structure that is observed around the W particles is likely to be WC. In addition, the diffraction peak of the W particle shows a significant shift to the left. This may be caused by the formation of a solid solution of C in the W grains. The elevated temperature of the carburizing treatment corresponds to an increased shift of the W phase diffraction peak to the left. Among the samples herein, the diffraction peak for the sample after carburization at 950 °C has the highest shift to the left, indicating that the degree of solid solution increases with increasing temperature. The XRD patterns of the sample after carburizing at 950 °C for 60, 120 and 180 min are shown in figure 4(b). It can be seen in the figure that the intensity of the WC diffraction peaks increases as the carburization time increases, indicating that an increased carburization time enables the C and W to react and form WC.

To analyse the changes in the relative contents of the different phases in the R2M tungsten alloy after carburizing treatment with different parameters, the XRD patterns of the R2M tungsten alloy obtained after the vacuum carburizing treatments are analysed semi-quantitatively. The XRD diffraction patterns of R2M tungsten alloy after carburizing are analysed with HighScore software. The analytical model is based on the semi-quantitative analysis algorithm associated with the Rietveld algorithm. The error range is controlled within 5%. Table 3 shows the specific values of the phase components of R2M for the carburizing time of 180 min and the carburizing temperatures of 850 °C, 900 °C, and 950 °C. The data in table 3 indicates that the relative content of the W phase after the vacuum carburizing treatment is lower than that of the original R2M W phase. This is because a large number of W atoms react with C atoms to produce carbides during the carburizing process, resulting in a decrease in the relative content of the W phase. Moreover, the relative content of W shows an elevated decrease at high temperatures because the activity of the C atoms increases with increasing
carburization temperature, and the effectiveness of the diffusion reaction of the C atoms and W phases also increases, so the relative content of the W phase in the sample at 950 °C is lower than that at 850 °C. At the same time, the relative content of WC and W\textsubscript{2}C (JCPDS file No. 20–1315) also increases with increasing temperature, indicating that an elevated temperature increases the relative content of the carbides and increases the impact of the carburizing process. Table 4 shows the specific values of the phase composition of the R2M tungsten alloy for the carburizing temperature of 950 °C and carburizing times of 60, 120, and 180 min. The analysis shows that a reduction in the W content is positively correlated with the carburization time, indicating that the W content decreases as the carburizing time increases. At the same time, the increase in the relative content of WC and W\textsubscript{2}C is also proportional to an increase in the diffusion time. This shows that an increase in the carburization time is

![Figure 4. XRD pattern of carburized samples at different temperatures (a) different temperatures for 180 min; (b) different times at 950 °C.](image-url)

| Temperature | Phase | WC  | W   | W\textsubscript{2}C | (Fe, Ni) |
|-------------|-------|-----|-----|------------------|----------|
| Original    |       | 0   | 96.2| 0                | 3.8      |
| 850 °C      |       | 50.9| 45.5| 1.2              | 2.4      |
| 900 °C      |       | 70.9| 24.3| 2.6              | 2.2      |
| 950 °C      |       | 65.1| 27.8| 6.5              | 0.7      |

Table 3. Relative content of surface layer of R2M carburized sample, % at 850 °C, 900 °C and 950 °C for 180 min.
helpful for the diffusion and reaction of C atoms; consequently, the carburization effect increases as the percolation time increases.

Based on the microstructure and XRD pattern analysis of the sample, it is concluded that the C layer on the surface of the sample mainly exists in the form of carbides, such as WC, and it adheres to the surface of the W particles. During the vacuum carburizing heat treatment, the active C atoms diffuse into the surface layer of the R2M alloy by atom diffusion under high-temperature conditions. Also, a fraction of the C diffuses into the binder phase, and the other part combines with the strong surface carbide comprising elemental W to form a stable carbide WC. This material adheres to the surface of the W particles, resulting in a decrease in the relative content of the W at the surface. At the elevated temperatures, the surface of the carburized sample is covered with additional carbides, the W phase content decreases, the diffusion depth increases, and the carburized layer increases [20]. As the carburization time is extended, a small amount of C reacts with WC to form W2C.

### 3.3. Influence of the carburizing process on the depth of the layer

Figure 5(a) shows the cross-sectional microstructure of a carburized R2M tungsten alloy sample after treatment at 900 °C for 120 min. It can be seen in figure 5(a) that the cross-section microstructure of the R2M sample after carburizing contains a black carburized layer, indicating that the carburizing treatment is effective for the R2M tungsten alloy. After carburizing, the microstructure contains three layers from the outside to the inside. The outermost layer is shown by the red ruler in the figure. The depth of this layer is approximately 30 μm. In this area, the outermost carburized layer can be clearly observed. A large number of carbide structures that surround the W particles and make them angular in shape are present; as shown by the blue scale in the subsurface region, the morphology of the W particles in this layer is not significantly changed, but a large amount of the black material appears in the subsurface region. These black regions are initially identified as the material carbonized by the vacuum carburization process that is surrounded by W particles. The depth of the subsurface layer was approximately 130 ~ 150 μm, indicating that the C element diffuses into this layer; the core structure remains almost unchanged and consistent with the original material. Figures 5(b), (c) shows the EDS spectrum sweep.

**Table 4.** Relative content of surface layer of R2M carburized sample/% at 950 °C for 60 min, 120 min and 180 min.

| Time  | Phase | WC  | W   | W2C | (Fe, Ni) |
|-------|-------|-----|-----|-----|---------|
|       | WC    | W   | W2C | (Fe, Ni) |
| Original | 0 | 96.2 | 0 | 3.8 |
| 60 min    | 47.2 | 48.9 | 3.1 | 0.9 |
| 120 min   | 49.9 | 44.7 | 3.6 | 2.3 |
| 180 min   | 65.1 | 27.8 | 6.5 | 0.7 |

**Figure 5.** Cross-sectional microstructure of the R2M after 900 °C, 120 min of surface carburizing (a) and EDS map of carburized sample treated (b), (c).
analysis of the R2M tungsten alloy sample after vacuum carburizing at 900 °C for 120 min from the carburized outer surface to the core. After the vacuum carburizing treatment, the C content in the surface layer increases significantly, and the carbon content of the surface of the sample after carburizing is significantly higher than that of the original sample surface. The relative content of C has gradient distribution, indicating that the relative content of the C element first decreases with an increase in the distance from the carburized outer surface of the sample and then stabilizes.

The outermost depth of the carburized layer in the R2M tungsten alloy obtained under different conditions is shown in figure 6. The figure shows that under the same carburizing time, as the carburizing temperature increases, the outermost layer depth of the carburized layer significantly increases. In addition, as the carburizing time increases, the outermost layer depth of the carburized layer also increases. When the carburizing time is 60 min, the outermost layer depth of the carburized layer is 48.35 μm, and when the carburizing time is increased to 120 min, the depth is increased to 63.24 μm. However, when carburizing for 180 min, the change in the outermost layer depth of the carburized layer is not obvious. Thus, it is observed that an increase in the depth of the outermost layer of the carburized layer is not linear. Because diffusion always spreads from a region with a high solute concentration to a region with a low solute concentration where the concentration difference is large, the diffusion rate is rapid. In the early stage of carburizing, the diffusion of C atoms is fast because of the large difference in the concentration. As the carburization time increases, the diffusion of C atoms into the matrix causes the concentration difference to decrease. Therefore, as the carburization increases with time, the depth of the outermost layer of the carburized layer increases, but the diffusion of the C atoms at prolonged times decreases, and the growth rate of the outermost layer depth of the carburized layer also decreases.

3.4. Effect of carburizing on surface hardness

The gradient hardness of the surface layer of the sample is shown in figure 7. The microhardness of the sample decreases with the increase in the distance from the carburized surface, and the hardness of the surface layer of the sample clearly decreases at approximately 200 μm, which is consistent with the results for the total depth of the outermost and subsurface layer of the carburized layer observed in the sample microstructure. The decreasing trend of the hardness values under the three temperature parameters is basically the same, and the hardness value of the surface carburized layer is much higher than the hardness value of the core. For the same carburizing time, the surface microhardness of the sample after vacuum carburizing at 950 °C is significantly higher than that of the samples treated at 900 °C and 850 °C, and the gradient hardness of the sample decreases relatively slowly, because at 950 °C, more C atoms react with W particles to form WC or W2C, resulting in the changes in the surface texture, thereby improving the surface hardness of R2M tungsten alloy; meanwhile, at the same carburizing temperature, the microhardness of the sample was highest at the carburizing time of 180 min. The surface hardness of the sample was the highest at the carburizing temperature of 950 °C and carburizing time of 180 min, and the hardness value was 396.43 HV. At the same carburizing time, the sample with the highest carburizing temperature has the highest hardness.

Figure 6. Relationship between different carburizing parameters and thickness of surface carburized layer after carburizing.
Figure 7. Microscopic gradient hardness of sample after vacuum carburizing heat treatment.
4. Conclusions

In this work, the microstructure, the depth of the infiltration layer and microhardness of the R2M alloy were studied before and after the vacuum carburizing treatment with different processing parameters. The following conclusions were drawn:

(1) After the vacuum carburizing treatment, the surface layer of the R2M tungsten alloy exhibits a carbide layer with a certain depth that can be divided into three layers: the outermost layer, the subsurface layer and the core layer. C in the carburized layer mainly adheres to the surface of the W particles in the form of WC, and its content increases with the increase in the carburizing temperature and time.

(2) The effect of the carburizing temperature and time on the carburizing effect of R2M is positive. Increasing carburizing temperature and prolonging carburizing time will increase the depth of the carburizing layer.

(3) The surface hardness of the R2M tungsten alloy can be improved significantly by the carburizing treatment, and the hardness value of the R2M tungsten alloy is increased from HV282 to 396HV, strengthening the surface of the R2M tungsten alloy.

Acknowledgments

This research was supported by the Ningbo Municipal Bureau of Science and Technology (2017B10031).

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