Study on High Temperature Oxidation Properties of Molybdenum-based Alloys

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Abstract. Research and design of different components of molybdenum-cobalt alloy, including Mo-3Co alloy, Mo-6Co alloy, Mo-9Co alloy and pure molybdenum alloy. The weight loss of pure molybdenum alloy, Mo-3Co alloy, Mo-6 Co alloy and Mo-9Co alloy at 400 °C, 600 °C, 800 °C, 1000 °C after 1-hour oxidation was systematically analyzed. Observing the surface of the oxide layer, it was found that the Mo-6Co alloy was vigorously oxidized at 800 °C and 1000 °C to form volatile MoO\textsubscript{3}. As the cobalt content increased, the weight loss rate of the samples showed a downward trend at different oxidation temperatures. Granular oxides were formed when the Mo-6Co alloy sample was oxidized at 400 °C; when oxidized at 600 °C, scaly oxides were formed; when oxidized at 800 °C and 1000 °C, blocky or flaky oxides were formed. Addition of the element of cobalt can obviously alleviate the oxidation of molybdenum-based alloy specimens at high temperature.

1. Introduction

With the development of ship technology, the service environment of the ships has changed, which puts forward higher requirements for the performance and preparation technology of the material. Known for its high strength and stability at high temperatures, molybdenum-based alloys are expected to replace nickel-based and aluminum-based alloys and serve as the new structural materials for ship development. The preparation of molybdenum-based alloys by traditional methods such as powder metallurgy and sintering technology will introduce impurity elements. Moreover, the preparation process is complex and there are limits to the shape of the formed parts [1-3]. In this paper, molybdenum-based alloys were prepared through selective laser melting method. As a result, the alloys are compact in structure and have good oxidation resistance. Among to the experimental results, the optimum preparation process was selected. The laser power was 325 W, the scanning speed was 400 mm/s, the thickness of powder laying was 30 µm, and the scanning distance was 40 µm [4, 5]. At this time, the sample formed had the largest density, which could reach 94.92%. Molybdenum has a high melting point and its workpieces is suitable for service at high temperature [6]. However, molybdenum metal is easily oxidized and volatilized at high temperature. The oxidation of molybdenum greatly limits the promotion and use of molybdenum alloys [7, 8]. The addition of cobalt can improve the oxidation resistance of molybdenum-based alloys and significantly reduce the
oxidation rate of molybdenum alloys [9].

2. Materials and methods
The test uses a QM-3SP4 planetary ball mill to thoroughly mix the two metal powders, and the grinding ball material is Al₂O₃. The powder mixing process is a dry milling of the ball material ratio of 1:1, the rotation speed of the ball mill is 300r/min, and the ball milling time is 20min. The mixed powder is placed in a 3C101-2A type Jindun electric furnace for drying. It was dried at 120 °C for 36 hours, then let it naturally cool down, and then the powder was subjected to selective laser melting forming.

The basic parameters of laser melting forming in the selection area are laser power of 325 W, scanning speed of 400 mm/s, powder thickness of 30 µm, and scanning pitch of 40 µm. Molybdenum-cobalt alloy parts containing 3%, 6% and 9% cobalt were prepared under these processing parameters, and their metallographic structure was analyzed. The oxidation experiments of the samples were carried out in RJX-8-13 high temperature box-type heating resistance furnace. The experimental temperatures were set as 400, 600, 800 and 1000 °C, respectively. The mass of the oxidized samples was measured after one hour of oxidation, and the weight loss curve of the oxidized samples was drawn. The surface morphology of the oxide layer was observed by Quanta 200 environmental scanning electron microscopy.

3. Results and discussion

3.1. Microscopic metallographic analysis
Figure 1 shows the metallographic structure of alloys formed by different compositions. Figure 1(a) shows the metallographic structure of pure molybdenum after 50 times magnification. The crystal grains are coarse, the grain size is not uniform, and there is no obvious crack. Figure 1(b) shows the metallographic structure of the Mo-3Co alloy formed by 50 times magnification, grain refinement, but obvious cracks were also found, and the cracks are mainly distributed at the overlap of adjacent melting channels, which indicates that the overlap of melting channels is easily cracked due to the influence of heat sources. It can be seen from figure 1(c) (d) that as the content of cobalt increases, the internal cracks of the alloy increase gradually, and the crack inside the Mo-9Co alloy is very obvious, which is related to the plasticity reduction of the alloy [10].

Figure 1. Metallographic structure of alloy parts with different composition
3.2. Oxidation kinetics of molybdenum-based alloys

The oxidation experiments of the samples were carried out in RJX-8-13 high temperature box-type heating resistance furnace. The mass of the samples was measured before high temperature oxidation of samples. The experimental temperatures were set respectively at 400 °C, 600 °C, 800 °C and 1000 °C, respectively. The mass of the oxidized samples was measured after one hour of oxidation, and the weight loss curve of the oxidized samples was drawn.

| Composition     | Oxidation temperature/°C |
|-----------------|--------------------------|
|                 | 400  | 600  | 800  | 1000 |
| Pure Mo         | 9.44 | 16.13| 24.03| 31.36|
| Mo-3Co          | 5.48 | 10.88| 14.58| 23.25|
| Mo-6Co          | 4.72 | 9.14 | 12.87| 20.62|
| Mo-9Co          | 4.18 | 7.42 | 11.83| 18.95|

It can be seen from the table that the weight loss rate of pure molybdenum samples is the highest at different oxidation temperatures. When cobalt is added to molybdenum, the weight loss rate of samples decreases greatly. The addition of cobalt can obviously alleviate the oxidation of molybdenum-based alloy samples at high temperature. With the increase of cobalt content, the weight loss rate of samples at different oxidation temperatures tends to decrease, but the change is not obvious. It can be seen that the average weightlessness rate of the samples increases obviously when the oxidation temperature increased from 800 °C to 1000 °C, which indicates that the oxidation phenomenon of the samples intensifies at 1000 °C.

3.3. Analysis of surface morphology of oxide layer

Before oxidation of the sample, the Archimedes drainage method was used to measure the density of molybdenum based alloys with different cobalt content, as shown in Table 2. It can be seen from the Table 2 that with the increase of cobalt content, the compactness of formed parts shows a significant downward trend. Under the same process conditions, the density of pure molybdenum parts is the highest, 94.92%. When 3% and 6% cobalt are added to the alloy, the compactness of the formed part decreases slightly, while when 9% cobalt is added to the alloy, the compactness of the formed part is 87.45%, with a large void ratio. In this paper, Mo-6Co samples with high density and molybdenum content were selected for further test.

| Composition of alloy | Density % |
|----------------------|-----------|
| Pure Mo              | 94.92     |
| Mo-3Co               | 92.18     |
| Mo-6Co               | 91.76     |
| Mo-9Co               | 87.45     |

It can be seen from the figure that the surface oxides of the samples at this time are less and generally in granular shape, and the spherical particles are distributed on the surface of the matrix, and the size of the oxides of Mo-6Co alloy samples is smaller and the number of oxides is less. The label of figure 2 (b) is enlarged and the position of particles is analyzed by EDS, as shown in figure 3 (a). It can be seen from the figure that the granular oxide is mainly composed of Mo, Co and O elements. The content of O element is 20.44%, that of Co element is 14.40%, and that of Mo element in matrix is 65.17%. The content of cobalt is lower than that of molybdenum, which indicates that most of the oxides are molybdenum oxides, while the content of
The oxides of pure molybdenum samples are scaly, small in size and unevenly distributed. In most areas, there are many scaly oxides stacked together. There are also some areas where the content of scaly oxides is less, while the original morphology of the matrix is maintained. The oxides of pure molybdenum samples are not dense enough. The oxides are easy to peel off from the matrix and some of the matrix are bare. The surface oxide layer cannot protect the inner metal, which leads to the continuous oxidation of the inner metal.

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Figure 2 (e) and (f) are the surface morphology of the oxide layer oxidized at 800 °C for pure molybdenum sample and the Mo-6Co alloy sample respectively. It can be seen from the figure that the morphology of the oxide layer at 800 °C of pure molybdenum sample is completely different from that of the oxide layer at 600 °C. The morphology of the oxide layer of the Mo-6Co alloy sample at 800 °C and the oxide layer at 600 °C share a similar morphology, but the size of the oxide at 600 °C is smaller than it is at 800 °C. From figure 2 (e), it can be seen that the oxide layer of pure molybdenum samples is flaky, the distribution of massive oxides is irregular, and there are many pores between oxides. It can be seen from figure 2 (f) that the size of oxide at 800 °C is obviously smaller than that at 600 °C. The label of figure 2 (f) is amplified and the position of oxide is analyzed by EDS, as shown in figure 3 (c). It can be seen from the figure that the oxide is mainly composed of Mo, Co and O. There are 30.17% of O element, 7.84% of Co element and 61.82% of Mo element in matrix. The content of cobalt is lower than that of molybdenum, which indicates that most of the oxides are molybdenum oxides, and the content of cobalt oxides is less.

Figure 2 (g) and (h) show the surface morphology of the oxide layer oxidized at 1000 °C for pure molybdenum and Mo-6Co alloy samples. It can be seen from the figure that the oxides of the two
alloys are in block or sheet shape, and the oxides are easy to peel off. The pure molybdenum sample has more oxide flake structure and larger pore space between oxides. The oxide size of Mo-6Co alloy sample is small, the pore size between oxides is small, and its distribution is more uniform and compact. It can be seen from figure 2 (h) that, compared with the pure molybdenum sample, after the surface metal is oxidized, the O element cannot easily entered into the alloy, so that the oxide layer can protect the internal metal.

![Image](image1.png)

**Figure 3.** High-magnification and energy spectrum analysis of the oxide layer on the sample
(a) Mo-6Co alloy 400 °C; (b) pure molybdenum 600 °C; (c) Mo-6Co alloy 800 °C

4. Conclusion
(1) With the increase of the content of cobalt in the molybdenum-cobalt alloy, the internal crystal grains of the material are refined, but the number of cracks increases, the crack size also increases, and the density of the formed parts shows a significant downward trend. Therefore, the cobalt element has
an effect on refining the inner crystal grains of the molybdenum material, but also on promoting the generation of internal cracks.

(2) With the increase of cobalt content, the weight loss rate of samples decreases at various oxidation temperatures. The addition of cobalt can obviously alleviate the oxidation of molybdenum-based alloy samples at high temperature.

5. References

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