The Effect of Deposition Time on The Properties of FeCrAl Coating on Molybdenum Alloy

Xi Sha*, An Geng, Zhang Xiao, Liu Ren-zhi, Wu Ji-na, Zhou Sha

Technical Center, Jinduicheng Molybdenum Co., Ltd, Xi’an 710077, Shaanxi, China
jszx@jdcmoly.com, xs19861105@126.com

Abstract: The FeCrAl coating was deposited on the surface of Molybdenum alloy by unbalanced magnetron sputtering, and the effect of deposition time on the composition, microstructure and properties of the coating was investigated. Characterized by XRD, SEM, German Standard (VDI3198(1991), indentation method) and ASTM C633-01 standard tensile analysis, the results show that the coating phase prepared at different deposition time is FeCrNi solid solution with BCC structure and the microstructure is ridge structure. With the increase of deposition time, the ridge structure on the surface of the film is more uniform, and its thickness increased from 21.6μm to 42.3μm. When the coating thickness is 42.3μm, the average bonding strength between the coating and the substrate is 39.7MPa, which meets the preparation requirements of the molybdenum alloy surface coating.

1. Introduction

As we all know, Molybdenum is widely used in electronic industry, mould manufacture and aerospace industry because of its high melting point, low coefficient of thermal expansion, good conductivity and good corrosion resistance[1-3]. Due to its brittleness at room temperature, high brittle-plastic transition temperature and easy oxidation at high temperature, its further application is limited to a great extent. At present, the plasticity, oxidation resistance and workability of molybdenum are improved by alloying treatment[4-6], but the alloying degree of molybdenum is very limited. The high temperature creep and thermal shock resistance of molybdenum alloys are greatly affected by the addition of alloying elements. Therefore, the method of improving the oxidation resistance of molybdenum alloy by alloying is limited. Another way to improve the high temperature oxidation resistance of molybdenum alloys is to prepare anti-oxidation protective coating on the surfaces of molybdenum and its alloys[7-10].

Chakraborty SP[11] prepared MoSi2 coating on TZM alloy by embedding method, and the MoSi2 coating has compact microstructure and high bonding strength with substrate. Guan Zhifeng[12] developed a glass based coating to prevent oxidation of molybdenum electrode in the furnace. The results of Majumdar S[13] show that Al doped silicide can form protective oxidation resistant coating on TZM alloy. Tang Dezhi[14] formed stainless steel coating on molybdenum substrate by magnetron sputtering. New research shows that, FeCrAl alloy has good oxidation resistance and low micro thermal neutron absorption cross section[15], so it can be used as a surface coating to reduce the oxidation rate of molybdenum alloy. Among the coating preparation technologies, magnetron sputtering is one of the most active research fields in materials science and engineering because of its dense, uniform and strong adhesion with the substrate.

FeCrAl coating was deposited on the surface of molybdenum alloy bars by four target closed field
unbalanced magnetron sputtering. The size of the substrate is 12×50mm. The effects of different deposition time on the microstructure, composition and properties of the coating were studied. We hope to find a way to improve the oxidation resistance of molybdenum alloy.

2. Experiment

FeCrAl coating was sputtered on molybdenum alloy bar by MSIP016 unbalanced magnetron sputtering equipment. Two 316L stainless steel targets (Fe content greater than 90 wt.%), one Cr target (purity 99.9 wt.%) and one Al target (purity 99.99 wt.%) were selected as sputtering targets. Two stainless steel targets are placed in opposite positions during the coating process, as shown in figure 1.

![Fig. 1 Layout structure of four targets](image)

Before coating, the molybdenum alloy bar was ultrasonically washed with acetone, alcohol and deionized water for 20min, 30min and 10min respectively, and then dried with nitrogen. The molybdenum alloy bar was quickly put into the sputtering equipment cavity. After vacuumizing to 5×10⁻⁵ pa, the molybdenum alloy bar was cleaned by back sputtering to remove the impurities and defects on the surface of the molybdenum alloy substrate. The sputtering gas was 99.999% high purity argon, the flow rate was 15sccm, the sputtering power was 2000W, and the sputtering time was 10min. Then the Cr target power was increased to deposit the base layer to ensure the bonding strength between the coating and the substrate, and the deposition time was 25 min. finally, the Al target and stainless steel target power were gradually increased to deposit the transition layer and working layer. Table 1 shows the deposition process parameters of FeCrAl coating. Keeping other sputtering parameters unchanged, FeCrAl coatings were prepared by changing the deposition time, and the effects of different deposition time on the microstructure and properties of the coatings were studied.

![Table 1 The deposition process parameters of FeCrAl coating](table)

The phase of the coating was analyzed with Bruker-AXS D8 x-ray diffractometer. The morphology and composition of the coating were observed with JSM-6700F field emission scanning electron microscope and energy dispersive spectrometer. The coating thickness was measured by JEOL JSM-7000F scanning electron microscope. The bonding strength was measured by German Standard (Vdi3198(1991), indentation method) and ASTM C633-01.
3. Results and Discussion

3.1 Effect of deposition time on thickness of coating

The thickness of FeCrAl coatings prepared at different deposition times is shown in Fig. 2. As can be seen from Fig. 2, the thickness of the coating increases with the increase of deposition time. The average thickness of the coating prepared with deposition time of 3h, 4h and 5h is 21.6μm, 25.9μm and 42.3μm respectively.

![Fig. 2 Diagram of relationship between coating thickness and deposition time](image)

3.2 Effect of deposition time on composition of coating

The types and contents of elements in FeCrAl coatings prepared at different deposition time were determined by EDS. The results are shown in Table 2.

| deposition time/h | Fe/wt%  | Ni/wt%  | Al/wt%  | Cr/wt%  |
|-------------------|---------|---------|---------|---------|
| 3                 | 64.84   | 6.06    | 6.02    | 23.04   |
| 4                 | 64.57   | 5.79    | 6.56    | 23.11   |
| 5                 | 64.75   | 6.18    | 6.13    | 23.05   |

It can be seen from Table 2 that the contents of Al, Fe, Cr and Ni in the coatings prepared at different deposition times have little difference. Figure 3 shows the XRD patterns of FeCrAl coatings prepared at different deposition times. It can be seen from Figure 3 that the FeCrAl coatings prepared at different deposition times are all polycrystalline. Compared with the standard PDF card, the phase of the coating is FeCrNi solid solution with BCC structure. The diffraction peaks in the figure increase with the increase of deposition time, indicating that the crystallization trend of the coating increases with the increase of deposition time. It can also be seen from Figure 3 that there is no diffraction peak of Al in the three coatings, which may be due to the existence of amorphous Al, which makes the diffraction peak broaden and the intensity weaken, or it may be due to the solid solution of Al into FeCrNi solid solution and the formation of a small amount of other intermetallic compounds, so that the diffraction peak of Al does not appear. Compared with the standard PDF card diffraction peaks, the diffraction peaks of FeCrNi solid solution of the three coatings all tend to shift to the left, which may be due to the solid solution of Al in FeCrNi solid solution, resulting in lattice mismatch and lattice distortion, which leads to the change of crystal face index. However, due to the change of crystallographic index, according to the Bragg equation, the diffraction peak of the coating will shift to a certain position. Secondly, with the decrease of vacuum chamber temperature after coating deposition, the difference of thermal expansion coefficient between FeCrAl coating and substrate results in the internal stress and the change of crystallographic index.
3.3 Effect of deposition time on microstructure of coating

Figure 4 and figure 5 show the cross section and surface morphology of FeCrAl coatings prepared at different deposition time.

It can be seen from Figure 4 that the cross-section morphology of the coating is columnar crystal structure. When the deposition time is 3h, the structure is still relatively fuzzy, and the columnar crystal structure becomes clear with the extension of deposition time.
As can be seen from Fig. 2, the surface morphology of the coatings prepared at different deposition times is similar, and the ridge structure gradually becomes relatively uniform with the increase of deposition time. The change of the micro morphology of the coating indicates that the deposition time has a great influence on the microstructure of FeCrAl coating. Because of the extension of the deposition time, the deposited atoms are fully diffused on the surface of the substrate, and the energy of the film formed by the first deposition is continuously obtained due to the continuous collision of the subsequent energy carrying particles, which makes the phenomenon of large grains swallowing small grains continue, and then the deposition process is completed. It promotes the crystallization of the film.

3.4 Effect of deposition time on adhesion strength of coating

Figure 6 shows the indentation morphology of FeCrAl coatings prepared at different deposition times. It can be seen from Fig. 6 that short radial cracks appear around the indentation of the coating deposited for 3 hours. The length of the cracks is less than 100 μm, and there are almost no circumferential cracks and local shedding around the indentation. This shows that the internal stress of the coating is lower and the bonding strength between the coatings and the substrate is better. With the increase of deposition time, the crack around the indentation gradually lengthens. When the deposition time is extended to 5h, the crack length around the indentation between the coating and the substrate is less than 200 μm, and the coating does not peel off. The results showed that the coating of 42.3 μm thick still bonded well with the substrate.

Four groups of coating samples with 5h deposition time were selected at random to test the bonding strength by tensile test. Fig. 7 is the drawing curve of four groups of samples. The tensile strength is 37.6 MPa, 41.5 MPa, 40.2 MPa and 39.6 MPa respectively, and the average strength is 39.7 MPa.
Fig. 7 Drawing of tensile strength of 4 coated samples prepared with deposition time of 5h

The bond strength of the AB adhesive used in the tensile test was about 60 MPa, while the maximum fracture strength of the coating was 41.5 MPa in four groups. The fracture positions of the four groups of samples were found at the interface of the coating and the substrate (Fig. 8). The fracture strength at this fracture location represents the bonding strength between FeCrAl coating and substrate. Therefore, the average bonding strength between the coating and the substrate was 39.7 MPa after 5 hours of deposition, which achieved the goal of this study (the coating thickness was 20 ~ 50μm, the bonding strength between the coating and the substrate was not less than 30 MPa).

Fig. 8 Macro-morphology of coated tensile specimen
(a) Pre-test sample; (b) Post-test sample

In addition, the fracture of the coating did not occur inside the coating under the test conditions. In combination with Fig. 4, it is shown that the FeCrAl coating deposited by magnetron sputtering process has good compactness and bonding strength, the invention can meet the preparation requirements of the molybdenum alloy surface coating.

4. Conclusion
1) The thickness of the deposited coating increases with the increase of deposition time, when the deposition time increases from 3h to 5h and the thickness of the film increases from 21.6μm to 42.3μm.
2) When the deposition time is changed, the phase of the deposited film will not be changed. The coating phase is FeCrNi solid solution with BCC structure, and the microstructure is cristae structure, but the cristae structure on the film surface is more uniform with the deposition time.

3) With the increase of the coating thickness, the bonding strength between the coating and the substrate is still good. When the coating thickness is 42.3μm, the average bonding strength between the coating and the substrate is 39.7 MPa.

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