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Electrochemical Preparation of Molybdenum Coatings on Nickel from KF-MoO_3 Melts

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In this paper, a molybdenum coating was first prepared in a molten KF-MoO_3 system by electrolysis, and the electrochemical behaviour of molybdenum ions in this system was studied at 900 °C. In the electrochemical test, a platinum wire was used as the working electrode, a molybdenum wire was used as the quasi-reference electrode and a graphite crucible was used as the auxiliary electrode. Results showed that the reduction process of molybdenum ions on a platinum electrode was a one-step process with an exchange of six electrons. The cathode process was a quasi-reversible process controlled by diffusion, and the diffusion coefficient was calculated to be 0.905×10^{-5} $cm^2\cdot s^{-1}$. Subsequently, galvanostatic electrolysis was carried out in the KF-MoO_3 (95:5 mol%) system, and a smooth and compact molybdenum coating was obtained. The influence of different electrolysis conditions on the quality of the molybdenum coating was also investigated. It is concluded that the coating quality was the best when the temperature was 900 °C, the current density was 11-33 $mA\cdot cm^{-2}$, the electrolytic time was 30-60 minutes, and the base material was nickel.

Keywords: molybdenum coating; electrodeposition; molten salt; fluoride

1. INTRODUCTION

Molybdenum is a rare refractory metal with excellent mechanical properties. It has been shown that the main advantages of molybdenum are its excellent physical properties and corrosion resistance at high temperatures [1]. Molybdenum is widely used in various industries, such as the metallurgical, electronics, and military industries [2], but this metal is difficult to prepare and very expensive. In industry, molybdenum ore is often calcined into molybdenum trioxide and then reduced by hydrogen or aluminium to obtain pure molybdenum. This process is expensive, and the subsequent treatment of the product is complex, which often requires reprocessing at high cost. In many cases, we focus on the surface quality of materials. If molybdenum metal can be used in the form of a surface coating, it may be a substitute for the use of bulk molybdenum.

Therefore, plating molybdenum on a substrate is a promising method to meet practical needs while reducing costs. At present, the common preparation methods of molybdenum plating include chemical vapor deposition, plasma spraying, fused salt electrolysis, etc. [3]. Compared with other methods, molten salt electrolysis has the advantages of a high current efficiency, high deposition rate, strong adhesion and good corrosion resistance [4]. The preparation of molybdenum coatings by molten salt electrolysis an older technique. In the 1950s, the electrodeposition of molybdenum from molten chlorides was achieved. Senderoff et al. [5] prepared a smooth and coherent molybdenum coating using a $LiCl$-KCl-K_3MoCl_6 fused salt system at 600 °C. Kolosov et al. [6] studied the electroplating of molybdenum on a nickel substrate. The experiment used $CaCl_2$-$CaMoO_4$-CaO as the melt to prepare a high-purity molybdenum coating suitable as the matrix material of a superconducting microwave system. Ene N et al. [7] achieved the electroplating of molybdenum from a $NaCl$-KCl-NaF-K_2MoO_4 system. The use of molten chlorides could result in problems, such as difficulty in preparing molybdenum chloride as the raw material and its susceptibility to impurities during the electroplating process. Therefore, a fluoride system has been studied and it seems to provide a better coating. Koyama et al. [8] obtained high-quality molybdenum coatings from a KF-$Na_2B_4O_7$-K_2MoO_4 system. Koyama et al. [9] also prepared a smooth molybdenum coating from KF-B_2O_3-K_2MoO_4 and determined the electrolysis conditions for obtaining a good coating. Terawaki et al. [10] reported the electrodeposition of molybdenum from a KF-B_2O_3-MoO_3 molten salt system and obtained a smooth molybdenum coating with good adhesion.

In this paper, a simple KF-MoO_3 molten salt system was first selected for electroplating molybdenum. The electrochemical behaviour of Mo^{6+} in this system was tested. In addition, we investigated the effects of current density, electrolysis time, temperature, pulsed currents and the type of substrate material on molybdenum plating. Notably, the results obtained from this electrolysis experiment differed from the conclusions of Terawaki et al. [10], who found that a molybdenum coating could not be obtained in a KF-MoO_3 system without the addition of B_2O_3.

2. EXPERMENTAL

KF (⩾99.5%) and MoO_3 (⩾99.95%) were kept at 200 °C for more than 48 h in an air atmosphere and under vacuum at 250 °C for 1 h to remove surface moisture. Then, the mixture was kept at 500 °C for 5 h and dried under a reduced pressure for 1 h. The experiments were performed in a graphite crucible located in an electric resistance shaft furnace in a pure argon atmosphere (⩾99.99%). The alumina tube inside the furnace was closed by the water-cooled, airtight heads on both ends. The experiment was carried out at 900 °C. A three-electrode system was used in the electrochemical test. The working electrode was a Φ1 mm platinum wire (⩾99.99%), the auxiliary electrode was a graphite crucible (spectrography), and the quasi-reference electrode was a Φ1 mm molybdenum wire (⩾99.9%). All electrodes were polished with sandpaper and rinsed with ethanol. For the electrolysis experiment, a molybdenum sheet (a width of 5 mm and a thickness of 0.5 mm, ⩾99.9%) was used as the anode. Nickel (a width of 5 mm and a thickness of 1 mm, ⩾99.9%) or copper (a width of 5 mm and a thickness of 1 mm, ⩾99.9%) plates were used as cathodes. The surface of the electrode sheet was polished with fine sandpaper to a mirror-like surface, degreased with acetone and then dried; finally, the electrode sheet was connected with a stainless-steel rod (SUS 304) for current collection.

The electrochemical behaviour of the molybdenum ions was tested by adding molybdenum trioxide at a concentration of 8.33×10^{-4} mol·cm^{-3}. Then, more molybdenum trioxide was added to reach a molar ratio of 5% for electrodeposition, and preelectrolysis was carried out for 3 h at a current density of 110 mA·cm^{-2} before electrodeposition. During electrodeposition, the effects of different current densities (11-77 mA·cm^{-2}), different electrolysis times (t=10-60 minutes), different electrolysis methods (direct current and periodic reverse current), different electrolysis temperatures (900 and 950 °C) and different base materials (Ni and Cu) on the quality of the molybdenum coating were investigated.

After electrolysis, the electrode was lifted up to the upper part of the furnace tube, where the temperature was relatively low. When it was sufficiently cooled down under the protection of argon gas, it was removed and washed in deionized water at a constant temperature of 50 °C for 10 minutes, soaked with acetone, and finally dried and weighed. In addition, after the experiment, the theoretical mass of the products was calculated according to Faraday's law, and the actual product mass was obtained by weighing the cathode plates before and after electrolysis. The current efficiency could be obtained from the ratio of the actual quality to the theoretical quality.

Both the cyclic voltammetry test and electrolysis were conducted by a PARSTAT 2273 potentiostat with Powersuite software (Princeton Applied Research, AMETEK). The composition and morphologies of the coatings were analysed by X-ray diffraction (Bruker D8 Advance; Bruker Corporation, Germany) and scanning electron microscopy with EDS (JSM-6510LV; JEOL).

3. RESULTS AND DISCUSSION

3.1. Cyclic voltammetry test and the preparation of the molybdenum coating

In the electrochemical test, a platinum wire was used as a working electrode, a molybdenum wire was used as a quasi-reference electrode and a graphite crucible was used as an auxiliary electrode. In the KF system at a temperature of 900 °C, the cyclic voltammograms before and after the addition of MoO_3 are shown in Fig. 1. The reduction potential of K^+ is observed at approximately -1.0 V, and there is no reduction peak in the potential ranges of -1.0~0.5 V. Therefore, the molten salt system can be used as a clean molten salt background. After the addition of MoO_3, one new pair of reduction/oxidation peaks (A/A') appear between -0.4 and 0.4 V, which should correspond to the deposition and dissolution of molybdenum, and its deposition potential is approximately -0.05 V in the system. There is a small peak before the reduction peak of molybdenum, which may be caused by impurities in the molten salt [11].

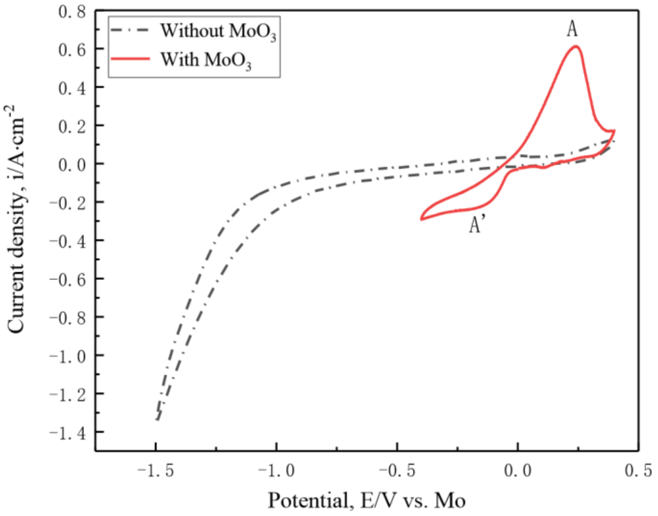


Figure 1. Cyclic voltammograms before and after the addition of MoO_3 (8.33×10^{-4} $mol\cdot cm^{-3}$) at a scanning rate of 0.1 $V\cdot s^{-1}$ on platinum in a KF molten salt at 900 °C.

The cyclic voltammograms at different potential scanning rates are recorded as shown in Fig. 2. The electrode potentials corresponding to anode peak currents show a slightly positive shift with the increase in scanning rate, and the electrode potentials corresponding to cathode peak currents show a slightly negatively shift. This result indicates that the cathode process is a quasi-reversible process.

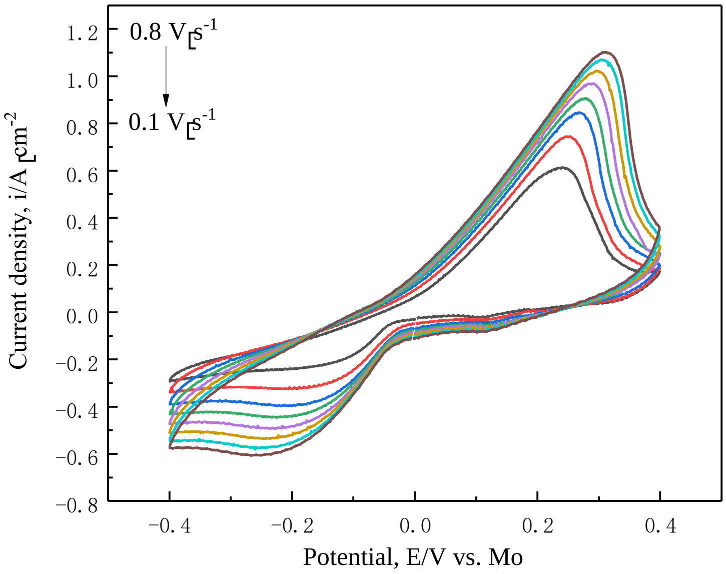


Figure 2. Cyclic voltammograms at different scanning rates on platinum in a KF-MoO_3 (8.33×10^{-4} $mol\cdot cm^{-3}$) molten salt at 900 °C.

Fig. 3 shows that the cathode peak current densities have a strictly linear relationship with the square root of the scanning rates. The fitted line passes through the origin and conforms to the Randles-Sevcik equation [12]. It is proven that the electrochemical reduction process of Mo^{6+} in the KF-MoO_3 system is diffusion-controlled. The relationship between the intensity of the cathode peak current and the potential scanning rate is in accordance with Equation (1) [13]. The value of the diffusion coefficient is calculated to be $D=0.905\times10^{-5}$ cm^2·s^{-1}. The electrochemical behaviour of molybdenum ions in a KF-B_2O_3-K_2MoO_3 system at 860°C has been investigated by cyclic voltammetry by Makytaet al. [14]. The results showed that the diffusion coefficient of molybdenum ions was 1.5×10^{-5} cm ^{2}·s^{-1}. The diffusion coefficient of molybdenum ions obtained by Li GX et al. [15] in a KF-B_2O_3-K_2MoO_3 system at 815 °C was $1.992.15\times10^{-5}$ cm^2·s^{-1}. Compared with these data, the diffusion coefficient of molybdenum ions in this paper is smaller, which may be because the addition of B_2O_3 accelerates the diffusion of molybdenum ions. nF $^{1/2}D^{1/2}v^{1/2}$ (1)

$$I_P=-0.61nFSC\left(\frac{nF}{RT}\right)^{1/2}D^{1/2}v^{1/2} \quad (1)$$

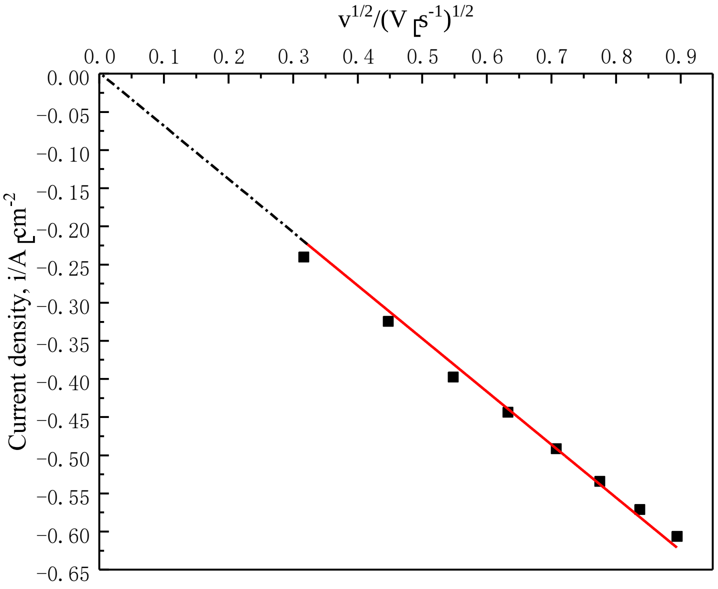


Figure 3. Relationship between the cathode peak current densities (I_{pc}) and the square roots of the scanning rate ($v^{1/2}$) from the cyclic voltammograms of Mo^{6+} on platinum in a $KFMoO_3$ (8.33× 10^{-4} mol·cm-3) molten salt at 900 °C.

Since the cathode process is a quasi-reversible process controlled by diffusion, the relationship between the current and potential conforms to Equation (2) [12]. The relationship between E and lg[(I_p-I)/I] for the reduction wave is provided in Fig. 4. According to the slope, the value of the transfer electron number (n) is calculated as approximately 5.7, so the reduction process of molybdenum ions on the platinum electrode is a reduction process with an exchange of six electrons, which is also consistent with the conclusions of Makyta M et al. [14].

$$E = B + \frac{2.3RT}{nF} lg \frac{I_p - I}{I} \quad (2)$$

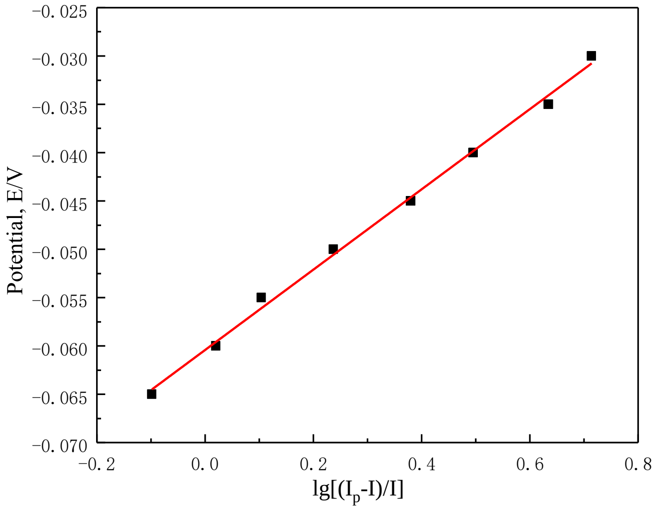


Figure 4. Relationship between E and lg [(I_p-I)/I] from cyclic voltammograms on platinum in a KF-MoO_3 (8.33× 10^{-4} mol·cm^{-3}) molten salt at 900 °C.

In the KF-MoO_3 (95:5 mol%) system, a molybdenum coating was successfully obtained on a nickel substrate by constant current electrolysis for 20 minutes at a current density of 33 mA·cm^{-2} at 900 °C. Fig. 5 shows the appearance of a nickel sheet (Fig. 5 (a)) and a molybdenum-plated nickel sheet (Fig. 5 (b)) for comparison. It is evident that the coating in Fig. 5 (b) with its metallic lustre is relatively uniform, which indicates that it is feasible to electroplate molybdenum on a nickel substrate in this system. This finding is different from the observations of Terawaki K et al. [10]. They believed that in a KF-MoO_3 system without B_2O_3, only powdered molybdenum, but not a molybdenum coating, could be produced.

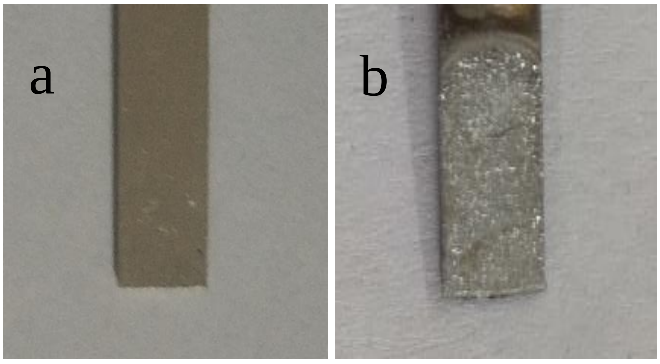
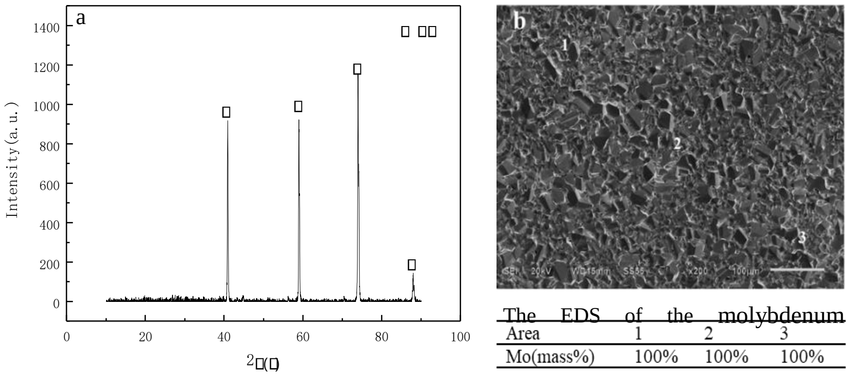


Figure 5. Comparison of the appearance of a nickel sheet (a) (before electrodeposition) and a molybdenum-plated nickel sheet (b) in the KF-MoO_3 (95:5 mol %) system by constant current electrolysis (33 mA·cm^{-2}) for 20 minutes at 900 °C.

The XRD result of the produced coating is shown in Fig. 6 (a), which demonstrates that the composition of the coating is molybdenum. The SEM-EDS results are shown in Fig. 6 (b). The surface of the coating is smooth and compact, and the purity of the molybdenum coating is 100%.



The EDS of the molybdenum			
Area	1	2	3
Mo(mass%)	100%	100%	100%

Figure 6. XRD pattern (a) and SEM-EDS image (b) of the molybdenum coating obtained in the KF-MoO_3 (95:5 mol %) system by constant current electrolysis for 60 minutes at a current density of 33 mA·cm^{-2} at 900 °C.

3.2. Effect of different current densities

The influence of different current densities on the surface morphology of coatings is studied. Fig. 7 (a)-(d) shows the SEM images of molybdenum coatings on nickel substrates at 900 °C at different current densities. Among them, the current density of 11 mA·cm^{-2} corresponds to a smoother and denser surface. As the current density increases to 33 mA·cm^{-2}, the grains gradually grow, and the surface flatness slightly decreases. When the current density reaches 55 mA·cm^{-2}, the grains become smaller.

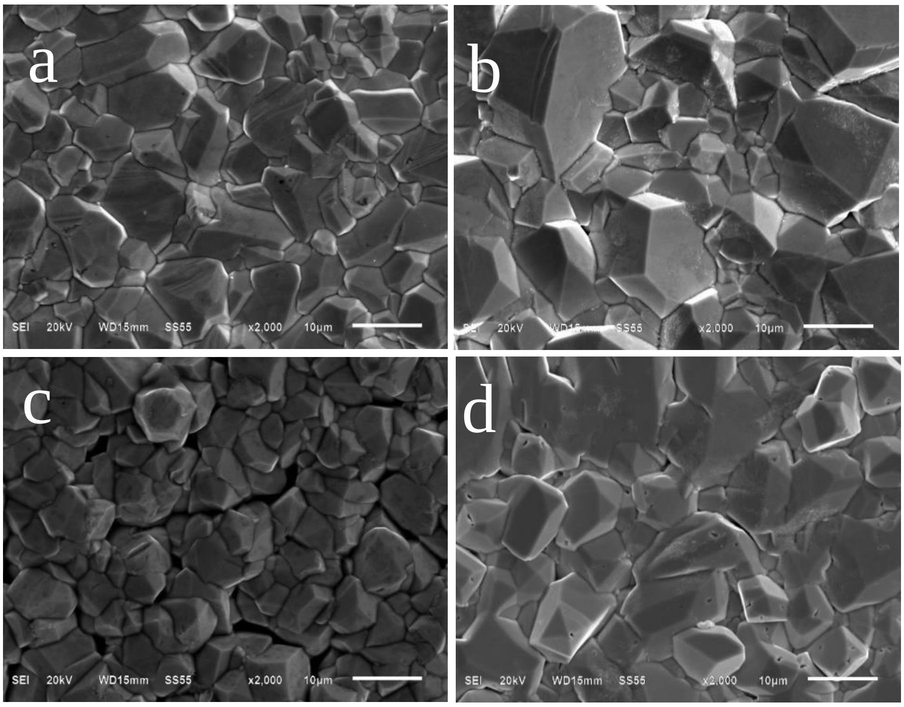


Figure 7. Effect of current density on surface morphology for electroplating molybdenum coatings in KF-MoO_3 (molar ratio 95:5, 60 min, 900 ℃): (a) 11, (b) 33,(c) 55, and (d) 77 mA • cm^{-2}.

A rough granular morphology gradually forms, and the number of surface voids clearly increase. Moreover, the current density of 77 mA·cm^{-2} corresponds to larger grain sizes, with few voids on the surface, which is an improvement compared with the surface at 55 mA·cm^{-2}. It is evident that the current density has a great influence on the grain size and flatness of the coating. When the current density is low, the number of nuclei is small, and the grain growth is slow, so the surface layer is dense and relatively flat. As the current density increases, the density of the nucleus increases, which refines the grains [16]. Grain growth is accompanied by the formation of nuclei, resulting in surface voids, which decrease the flatness. After continuing to increase the current density, the rapid growth of grains makes the surface coverage more uniform, but the generation of pores cannot be avoided. Overall, the current density of 11-33 mA·cm^{-2} is the optimum condition for this system at 900 °C. A lower current density has a positive effect on the production of flat and dense coatings, while a high current density increases the nucleation density. Therefore, nucleation at high currents and growth at low currents facilitate the formation of high-quality coatings [17,18].

The cross-sectional micrographs of molybdenum coatings at different current densities are shown in Fig. 8 (a)-(d). The left side faces the anode, and the right side is the reverse side. When the current density is 11 mA·cm^{-2}, the thickness of the coating is 6 μm. When the current density reaches 33 mA·cm^{-2}, the thickness increases to 15 μm. In Fig. 8 (a) and (b), the plating layer is tightly bonded to the nickel substrate, and the compactness of the coating is good. However, the continuous increase in the current density (55 mA·cm^{-2} and 77 mA·cm^{-2}) does not increase the thickness of the coating on the left side. The front of the coating becomes thinner, and the thickness of the reverse side increases. Dendritic products are observed on both sides of the coating at 55 mA·cm^{-2}. When the current density is 77 mA·cm^{-2}, the plating layer seems to be smoother. A few voids are observed in the cross-section of the coating, which is consistent with that observed from the surface morphology in Fig. 7 (d). At a small current density, the nucleation rate is slow, and the grains are sufficiently grown, so the observed coating is smooth and continuous. With increasing current density, a large number of nuclei are formed on both the front and back surfaces of the electrode at the same time, which decreases the thickness of the coating on the front side of the electrode. In addition, the high current density makes the morphology of the coating tend to be dendritic, and the grains grow preferentially in the protruding part, which makes the thickness of the coating in each area less uniform than that at the low current density [19]. When the current density increases to 77 mA·cm^{-2}, the smoother coating may be due to dendrites falling off, which can also be proven by the calculation results of the current efficiency discussed below. From the thickness and uniformity of the coating, the optimum current density is 33 mA·cm^{-2}.

The effect of current density on current efficiency is shown in Fig. 9. From the perspective of cathode current efficiency, the current efficiency decreases as the current density increases, which seems to be due to the acceleration of the deposition rate at a high current density; this increased deposition rate results in the failure of powdered molybdenum or dendritic molybdenum that easily falls off to adhere to the cathode surface [20]. Some powdered molybdenum metals are also collected in the electrolyte after electrolysis. In terms of energy consumption, the recommended current density is also 11-33 mA·cm^{-2}.

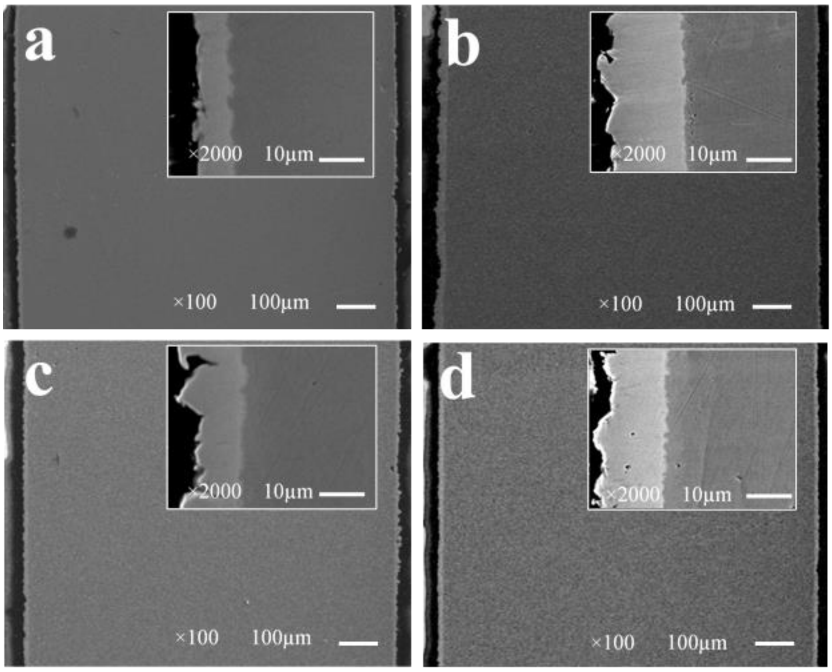


Figure 8. Effect of current density on Cross-sectional morphologies for electroplating molybdenum coatings in KF-MoO_3 (molar ratio 95:5, 60 min, 900 ℃): (a) 11, (b) 33,(c) 55, and (d) 77 $mA\cdot cm^{-2}$.

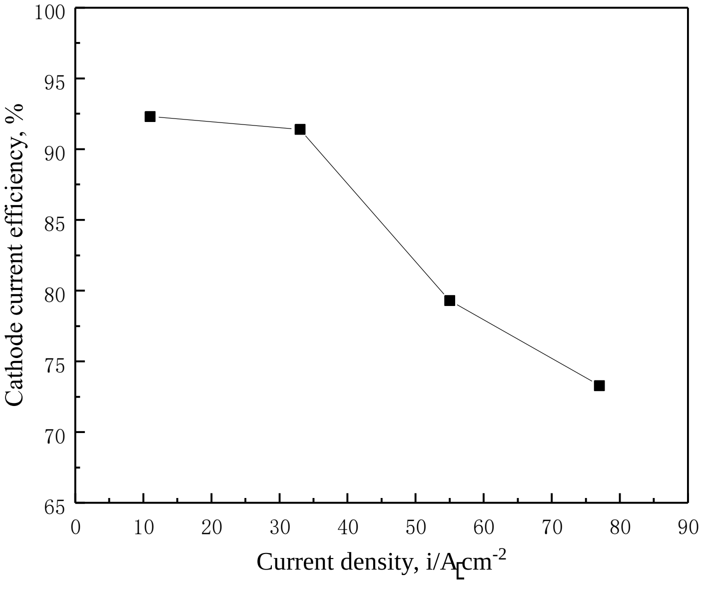


Figure 9. Effect of current density on cathode current efficiency for electroplating molybdenum coatings in KF-MoO_3 (molar ratio 95:5, 60 min, 900 ℃).

3.3. Effect of the electrolysis time

For determining the growth process of molybdenum coatings, the changes in the surface morphology corresponding to different electrolysis times were also explored. As shown in Fig. 10 (a)-

(d), when the electrolysis time is 10 minutes, nuclei form, but the grain growth is insufficient, the grain size is not uniform, and the surface grains do not cover the entire substrate. When the electrolysis time is increased to 20 minutes, the surface of the substrate is covered with a complete and compact coating layer. When the time is increased to 30 minutes, the coating remains smooth and compact, and the grain size gradually increases. After 1 h of electrolysis, the grain size clearly increases. The particle size tends to be inhomogeneous, but the coating is still smooth. At the initial stage of electrolysis, the grain size is small, and the grains grow unevenly on the substrate, forming a bumpy morphology, as shown in Fig. 10 (a). With increasing time, the grains grow sufficiently and gradually cover the whole surface of the substrate, and the coating layer tends to be dense and compact (Fig. 10 (b) and (c)). At the later stage of electrolysis, the grains grow along the preferential orientation, leading to a nonuniform grain size (Fig. 10 (d)). If the electrolysis time is continuously increased, dendritic products form, but a short electrolysis time does not lead to the formation of dendritic products [21]. Therefore, we suggest that the optimum time for molybdenum plating on nickel substrates is 30-60 minutes when the current density is 33 mA·cm^{-2} and the temperature is 900 °C.

The current efficiency is also calculated as shown in Fig. 11. The result indicates that the electrolysis time has little effect on the current efficiency. The current efficiencies corresponding to 30 and 60 minutes are almost the same, both exceeding 90%. The cathodic current efficiencies corresponding to 20 and 10 minutes exceed 100%, which may be caused by a small amount of salt residue in the surface pores.

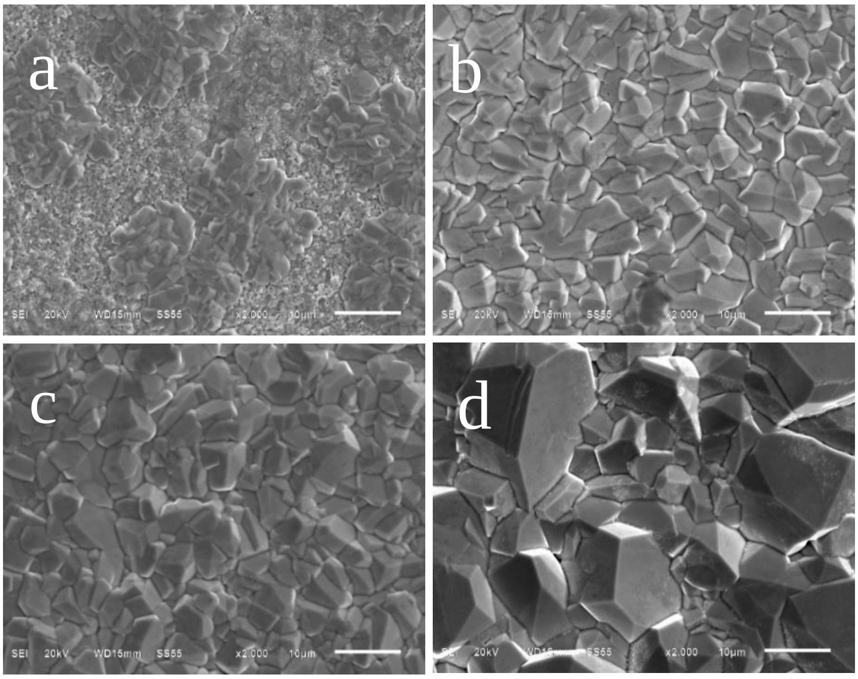


Figure 10. Effect of electrolysis time on surface morphology for electroplating molybdenum coatings in KF-MoO_3 (molar ratio 95:5, 33 mA·cm^{-2}, 900 ℃): (a) 10, (b) 20, (c) 30, and (d) 60 minutes.

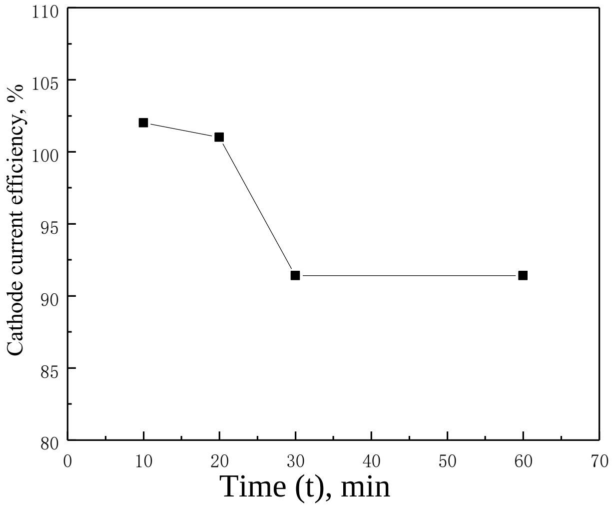


Figure 11. Effect of electrolysis time on cathode current efficiency for electroplating molybdenum coatings in KF-MoO3 (molar ratio 95:5, 33 mA • cm-2, 900 ℃).

3.4. Effect of other electrolysis conditions

In addition to the effects of current density and electrolysis time during electrolysis, temperature is also an important parameter affecting the coating. Fig. 12 (a) and (b) show the surface topography of the coatings at 900 °C and 950 °C, respectively. The grain size decreases and becomes more uniform with increasing temperature, but fine pores appear, resulting in a less dense plating layer and a decrease in surface flatness. From the comparison of the cross-sectional morphologies (Fig. 13 (a) and (b)), the temperature increase has an effect on the thickness of the coating. At 950 °C, the coating grows on both sides of the front and back, and obvious dendritic products are observed in the coating, which results in a significant decrease in the consistency of the coating. Therefore, we believe that temperature has a positive effect on refining the grain size. The number of crystal nuclei at high temperatures is higher than that at low temperatures, but the grain growth is insufficient, resulting in porosity. Under the conditions used in the experiment, it is recommended to set the temperature at 900 °C.

In constant current electrolysis, crystal grains often grow in a preferential orientation, which is more likely to produce dendritic or even powdery products. Periodic reverse current technology endeavours to improve the coating. Specifically, after electrolysis for a certain period of time, the same anode current as the cathode current is applied to the substrate, which lasts for a shorter period of time and is repeated for multiple cycles [22]. In this experiment, when the current density is 33 $mA\cdot cm^{-2}$, forward electrolysis lasts for 18 s, and then electrolysis is reversed for 9 s; this sequence is repeated for 400 cycles. The product morphology comparison of different electrolysis methods (direct current/periodic reverse current) is shown in Fig. 12 (a) and (c). The surface flatness of the coating obtained by the periodic reverse current method is clearly improved, and the grain size is relatively small and uniform. When the particles are preferentially grown to produce grain bumps, the applied reverse current dissolves the surface protrusions, making the surface of the coating very flat and the grains finer [23]. Comparing the sectional views under different electrolysis conditions (Fig. 13 (a) and (c)), the layer obtained by the periodic reverse current is flat and dense. Some areas are defective, and the thickness of the coating decreases, which may be related to improper parameter settings. Parameters, such as the current density and duration of reverse current, are important factors. Overall, the method is very effective in improving the quality of the coating, but it consumes more energy and time.

In addition to nickel, copper was also selected as a substrate for plating. The surface morphologies of the molybdenum coating on the different base materials are shown in Fig. 12 (a) and (d). Smooth and compact coatings can also be obtained by using copper sheets as substrates. However, the preferred orientation of grains on the copper substrate is more obvious, and it is easy to produce dendritic products after long-term electrolysis. When observing the cross-section of molybdenum coatings on the different substrates (Fig. 13 (a) and (d)), it is found that the adhesion of the coating on the copper substrate is weak, and there are obvious gaps between the plating and substrate in some areas. The thickness of the coating on the copper substrate is thinner than that on the nickel substrate, which may be caused by the shedding of dendrites. It is also noted that in the experiment, the stability of the copper sheet in the system is insufficient, and there is little dissolution during the electrolysis process. If the copper sheet is used as the base material, the electrolyte can be slightly contaminated.

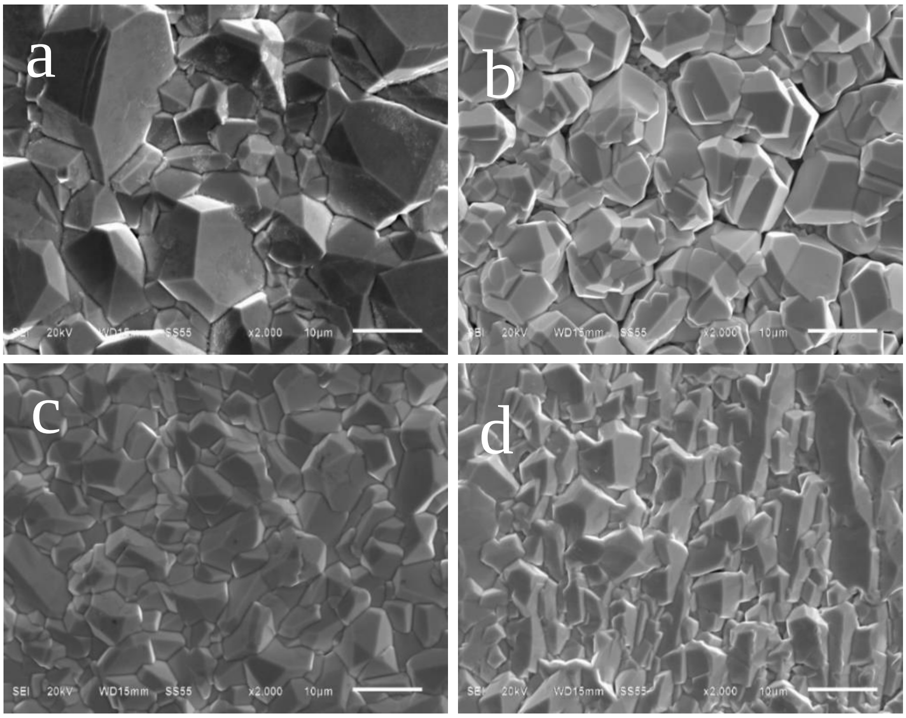


Figure 12. Effect of different electrolytic conditions on surface morphology for electroplating molybdenum coatings in KF-MoO$_3$ (molar ratio 95:5): (a) 900 °C, nickel substrate, 33 mA·cm^{-2}, and 60 minutes; (b) 950 °C, nickel substrate, 33 mA·cm^{-2}, and 60 minutes; (c) 900 °C, nickel substrate, 33 mA·cm^{-2}, and periodic reverse current (t_c = 18 s, t_a = 9 s, 400 cycles); and (d) 900 °C, copper substrate, 33 mA·cm^{-2}, and 60 minutes.

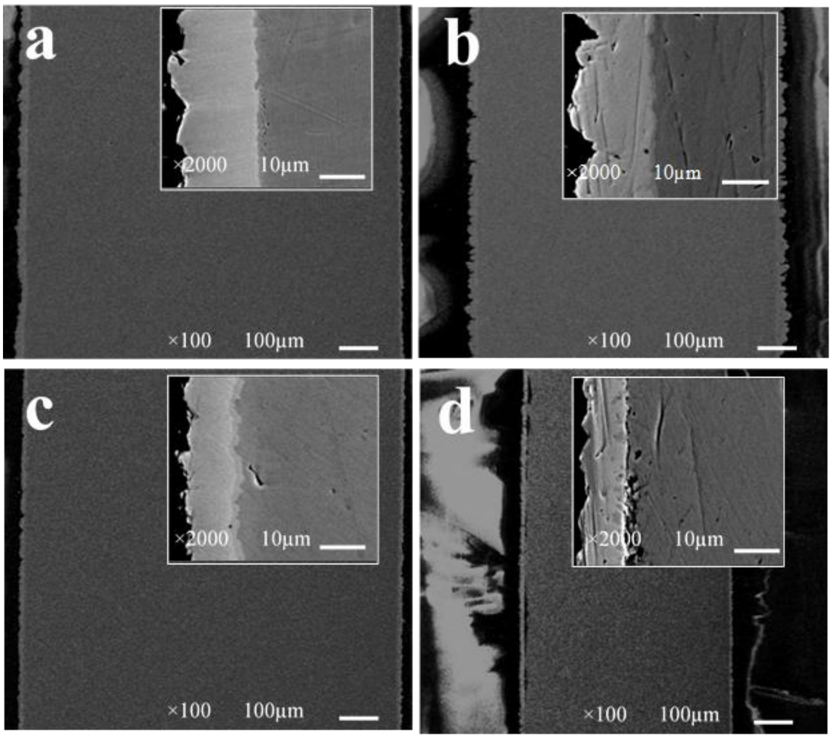


Figure 13. Effect of different electrolytic conditions on Cross-sectional morphologies for electroplating molybdenum coatings in KF-MoO_3 (molar ratio 95:5): (a) 900 °C, nickel substrate, 33 mA·cm^{-2}, and 60 minutes; (b) 950 °C, nickel substrate, 33 mA·cm^{-2}, and 60 minutes; (c) 900 °C, nickel substrate, 33 mA·cm^{-2}, and periodic reverse current (t_c = 18 s, t_a = 9 s, 400 cycles); and (d) 900 °C, copper substrate, 33 mA·cm^{-2}, and 60 minutes.

Table 1. Effect of different electrolytic conditions on Cathode current efficiencies for electroplating molybdenum coatings in KF-MoO_3 (molar ratio 95:5).

Temperature	Electrolysis method	Current density	Electrolysis time	Substrate material	Current efficiency
900°C	Constant current	33 mA·cm^{-2}	60 minutes	Ni	91.4%
950°C	Constant current	33 mA·cm^{-2}	60 minutes	Ni	91.4%
900°C	Periodic reverse current	33 mA·cm^{-2}	180 minutes	Ni	79.1%
900°C	Constant current	33 mA·cm^{-2}	60 minutes	Cu	60%

The cathode current efficiencies under these electrolysis conditions are provided in Table 1. The temperature has little effect on the current efficiency, and the current efficiency when using the periodic reverse current is lower, which may be related to improper parameters. The current efficiency for using the copper substrate is only 60% because the obvious preferential orientation of molybdenum deposition on a copper substrate makes it easier to produce dendritic structures, thereby resulting in lower current efficiency.

4. CONCLUSIONS

By studying the electrochemical behaviour of molybdenum ions in the KF-MoO_3 system and the electroplating of molybdenum in the system, we come to the following conclusions:

(1) Cyclic voltammetry tests show that the reduction process of molybdenum ions on a platinum electrode is a one-step process with an exchange of six electrons. The cathode process is a quasi-reversible process controlled by diffusion, and the diffusion coefficient is calculated to be 0.905×10^{-5} $cm^2\cdot s^{-1}$.

(2) By investigating the influences of different electrolysis conditions on the molybdenum coatings, it has been found that in the KF-MoO_3 system, molybdenum coatings can be obtained on both nickel and copper substrates, but plating on the nickel substrate is better. The optimum electrolysis temperature is 900 °C. When the current density is controlled within the range of 11-33 $mA\cdot cm^{-2}$, the plating layer is flat and dense, and the recommended electrolysis time is 30-60 minutes. The current efficiency is optimal when depositing molybdenum on a nickel substrate at current densities of 11-33 $mA\cdot cm^{-2}$. In addition, high-current nucleation and small-current growth can be used to obtain better quality coatings. Finally, if energy consumption is not considered, the quality of the coating obtained by the periodic reverse current method under proper parameters is very good.

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