

Article

Preparation of Molybdenum Coatings by Molten Salt Electrodeposition in $\text{Na}_3\text{AlF}_6\text{-NaF-Al}_2\text{O}_3\text{-MoO}_3$ System

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Abstract: In this paper, electrodeposition of a molybdenum coating was conducted in $\text{Na}_3\text{AlF}_6\text{-NaF-Al}_2\text{O}_3\text{-MoO}_3$ molten salts at 930 °C to investigate the availability of preparation of thick molybdenum coatings. The effects of current density and electrodeposition time on the morphology of the produced molybdenum coating were studied. With the increase of current density ($10\sim70\text{ mA}\cdot\text{cm}^{-2}$), the coating thickness was increased from 10 μm to 30 μm , with all the current efficiency above 97%. Under a current density of $30\text{ mA}/\text{cm}^2$, with the rise of electrodeposition time ($10\sim60\text{ min}$), three stages of the deposit growth were observed, including the formation of a large number of fine crystals, transformation into fibrous morphology and well-developed faceted grains. The formation of a large number of fine crystals at the initial stage of the electrodeposition could facilitate electroplating molybdenum coatings with good quality at higher current density and longer duration. Thus electrodeposition at a current density of $100\text{ mA}\cdot\text{cm}^{-2}$ for 3 h has been performed, resulting in the preparation of relatively flat, dense, and coherent molybdenum coatings with a thickness of 140 μm on a nickel substrate, with a current efficiency above 85%. It is anticipated that the electrodeposition of molybdenum coatings in the present molten system is suitable for electroplating thick molybdenum coatings.

Keywords: cryolite-based molten salt; electrodeposition; molybdenum coating; nickel substrate



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1. Introduction

Molybdenum (Mo) possesses excellent properties, such as high thermal and electrical conductivity, high modulus of elasticity, high strength at elevated temperatures, and good resistance to corrosion [1,2], which make it a suitable candidate for high-temperature applications, the automotive industry, and space application [2,3]. However, it is very expensive and difficult to fabricate, so it is worthwhile to establish a technique to coat inexpensive metal substrates with molybdenum [4,5].

Molybdenum coatings are often produced by means of thermal spraying [6–8], low-pressure plasma spraying [9], and chemical vapor deposition (CVD) [10,11]. These spraying methods, however, involve high manufacturing costs associated with the use of specialized equipment to provide a vacuum environment [6–9]. For the CVD method, the process is generally accompanied by the volatile reaction between byproducts and the unused precursor species [11,12].

Molten salt electrodeposition is an attractive method to fabricate molybdenum coatings because of its simple techniques and capability to cover complex surfaces. The preparation of molybdenum coatings by molten salt electrolysis began in the 1950s [13]. Up to now, the applied types of molten salts are classified into four groups: (1) chloride fused salts [14–16], (2) fluoride fused salts [17–20], (3) oxide fused salts [21], and halide-oxide fused salts [22]. The use of molten chlorides or fluorides has the disadvantage of difficulty in preparing molybdenum chloride or fluoride as raw materials. Therefore, researchers pay more

attention to molten fluoride-oxide systems, where it seems that molybdenum coatings with better quality could be provided. Among these systems KF-based fluoride-oxide molten salts have been mostly investigated to produce molybdenum coatings on various substrates [18–20,23].

It is noted that parameters such as cathode current density and electrolysis time mainly affect the quality of the coating. It is worth mentioning that molten salt electrodeposited coatings tend to grow into dendritic or powder form at high cathode current densities, so the preparation of thick metallic molybdenum coatings has been considered to be challenging [24–26]. The thickness of molybdenum coating determines its performance and service life. In military, aerospace, nuclear industry, and other application fields, it is necessary to prepare a molybdenum coating with a thickness of more than 100 μm [2]. In addition, compared with KF, cryolite is relatively inexpensive and easy to be attainable.

Therefore, in this paper, for the first time, the cryolite-based melt was selected for the exploration of the electrochemical deposition of thick molybdenum coatings. In Na_3AlF_6 - NaF - Al_2O_3 - MoO_3 molten salts at 930 $^\circ\text{C}$, the effects of current density and electrolysis time on the produced metallic molybdenum coatings were investigated. Moreover, we attempt to prepare dense and flat molybdenum coatings with a thickness of more than 100 μm at large current densities of more than 100 $\text{mA}\cdot\text{cm}^{-2}$.

2. Experimental

2.1. Raw Material and Experimental Setup

The raw materials used in the experiment are Na_3AlF_6 ($\geq 99\%$, Sinopharm, Shanghai, China), NaF ($\geq 99.5\%$, Aladdin, Shanghai, China), Al_2O_3 ($\geq 99.95\%$, Aladdin, Shanghai, China), and MoO_3 ($\geq 99.95\%$, Shanghai, China). They were kept in a drying oven at 200 $^\circ\text{C}$ for 48 h to remove surface moisture before use. During the electroplating process, a two-electrode system was applied. The anode was a molybdenum sheet ($8 \times 3 \times 50$ mm) ($\geq 99.9\%$, Haoye, Xingtai, China). The cathode was a nickel sheet ($4 \times 1 \times 25$ mm) ($\geq 99.9\%$, Shuanghua, Xingtai, China). The surface of the electrode was polished with fine sandpaper to mirror the surface, rinsed with acetone, and dried, and then the prepared electrode was connected to a molybdenum rod acting as a current collector.

2.2. Coating Operation

The experimental setup for the preparation of metallic molybdenum coatings by electrodeposition in Na_3AlF_6 - NaF - Al_2O_3 - MoO_3 system is shown in Figure 1. Na_3AlF_6 and NaF were added into the graphite crucible at a mole ratio of 21:79 and then heated to 930 $^\circ\text{C}$ and melted in the vertical electric resistance furnace. Then, MoO_3 and Al_2O_3 were added into the Na_3AlF_6 - NaF molten salts with a content of 5 mol % and 0.015 mol %, respectively. The electrodes were inserted into the molten salts and pre-electrolysis experiments were carried out at a current density of 110 $\text{mA}\cdot\text{cm}^{-2}$ for 2.8 h to remove impurity elements from the molten salts. After the pre-electrolysis, the effects of current density (10 $\text{mA}\cdot\text{cm}^{-2}$, 30 $\text{mA}\cdot\text{cm}^{-2}$, 50 $\text{mA}\cdot\text{cm}^{-2}$, and 70 $\text{mA}\cdot\text{cm}^{-2}$) and electrolysis time (10 min, 20 min, 30 min, and 60 min) on the morphology of the prepared molybdenum coatings on nickel substrates were studied in Na_3AlF_6 - NaF - Al_2O_3 - MoO_3 system. Subsequently, electrodeposition was performed at current densities of 100 $\text{mA}\cdot\text{cm}^{-2}$ and 300 $\text{mA}\cdot\text{cm}^{-2}$ for 3 h and 1 h, respectively, to produce thick molybdenum coatings at higher current densities and longer electrolysis time. All the electrodeposition experiments were performed under an argon atmosphere. A DC power supply (HLR-3660D, Henghui, Shenzhen, China) was used to perform the galvanostatic control.

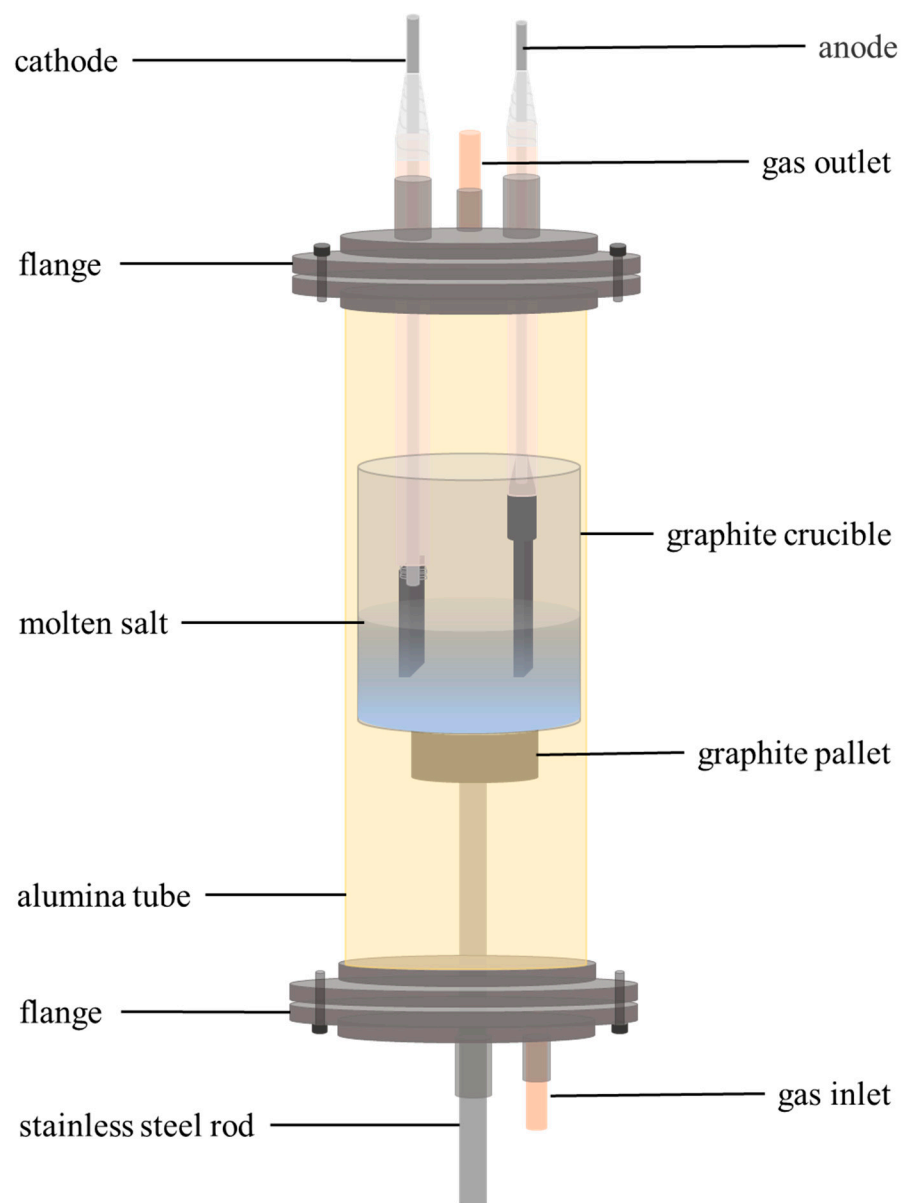


Figure 1. Schematic diagram of the experimental setup for the preparation of metallic molybdenum coatings by electrodeposition in $\text{Na}_3\text{AlF}_6\text{-NaF-Al}_2\text{O}_3\text{-MoO}_3$ salts at 930°C .

2.3. Characterization

After the electrodeposition experiment, the coated nickel substrates were removed and cooled, cleaned ultrasonically in deionized water for 10 min, then rinsed and soaked in acetone to remove the surface water, dried, and weighed. The surface and cross-section morphologies of the molybdenum metal coatings were examined using scanning electron microscopy equipped with energy dispersive spectroscopy (SEM-EDS, JSM-6510LV, JEOL, Tokyo, Japan). X-ray diffraction (XRD, Smart Lab, Rigaku, Tokyo, Japan. voltage: 40 kV, current: 40 mA, scan rate: $10^\circ/\text{min}$) was used to identify the phase composition of deposits on nickel substrates. After the electrolysis, the cathode current efficiency (η) was calculated by the following equation:

$$\eta = \frac{m}{qIt} \times 100\% \quad (1)$$

where m is the mass of molybdenum coatings, q is the electrochemical equivalent, I is the cathode current, and t is the electrolysis time.

3. Results and Discussion

In the $\text{Na}_3\text{AlF}_6\text{-NaF-Al}_2\text{O}_3\text{-MoO}_3$ system at 930°C , electrolysis was carried out at a cathode current density of $30\text{ mA}\cdot\text{cm}^{-2}$ for 60 min, with the photograph of the produced coating with metallic luster shown in the top-left of Figure 2a, which was identified as molybdenum from the XRD results in Figure 2a. The surface morphology of the molybdenum coating is shown in Figure 2b, which was flat and uniform. And the EDS analysis (bottom-right of Figure 2b) revealed the high purity of the produced molybdenum coating.

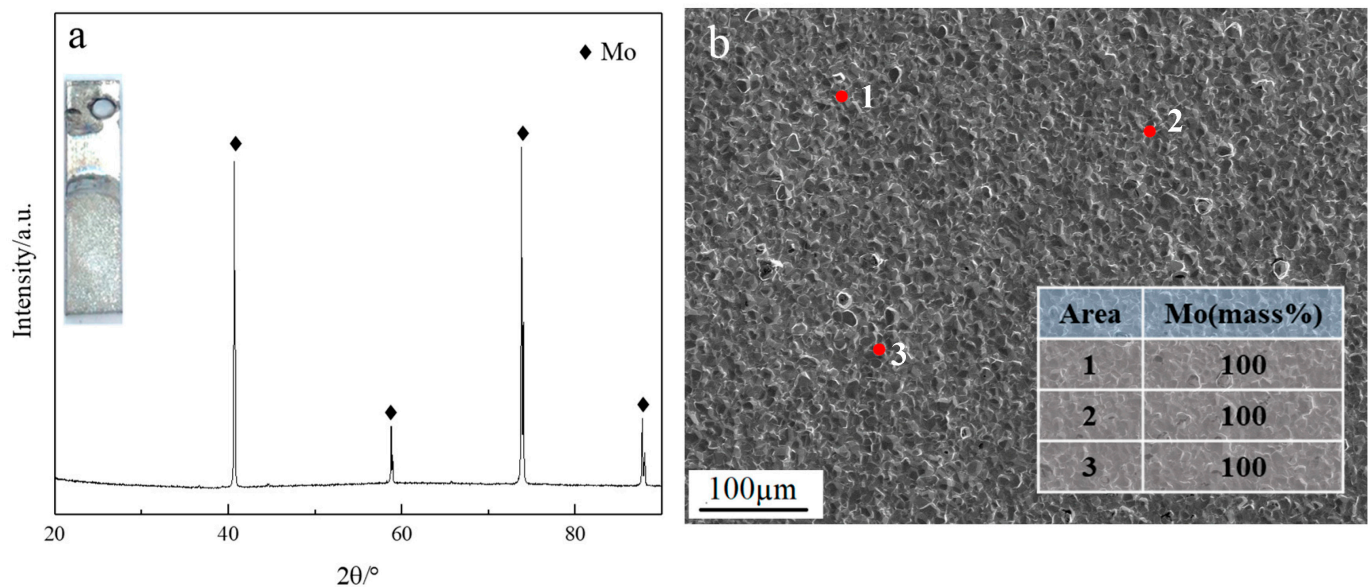


Figure 2. The appearance, XRD patterns (a), and SEM-EDS (b) of molybdenum coating obtained in $\text{Na}_3\text{AlF}_6\text{-NaF-Al}_2\text{O}_3\text{-MoO}_3$ system by constant current electrolysis for 60 min at a current density of $30\text{ mA}\cdot\text{cm}^{-2}$ at 930°C .

3.1. Effect of Current Densities on Molybdenum Coatings

The effect of current density ($10\sim 70\text{ mA}\cdot\text{cm}^{-2}$) on the produced molybdenum coatings was studied, and the surface morphologies are shown in Figure 3.

At the current density of $10\text{ mA}\cdot\text{cm}^{-2}$, the grains on the surface of the molybdenum coating were relatively fine. As the current density increased to 30 and $50\text{ mA}\cdot\text{cm}^{-2}$, the grain size became larger and more uniform, and the grain bonding was compact without voids and holes. When the current density reached $70\text{ mA}\cdot\text{cm}^{-2}$, there were obvious coarse grains on the surface of the deposition layer with decreased flatness. There were voids between the grains and a few holes on the grain surface. Therefore, from the observation results of the surface morphology of the deposited molybdenum coating shown in Figure 3, when the current density was small, better uniformity and flatness of the surface were presented.

According to the basic principle of electrochemical deposition, when the current density is small, the low energy supply for the nucleation and growth results in low nucleation and grain growth rates. Thus, the formed coating is compact and relatively flat, which corresponds to the surface morphologies of produced molybdenum coatings at current densities from 10 to $30\text{ mA}\cdot\text{cm}^{-2}$. When the current density increases to $70\text{ mA}\cdot\text{cm}^{-2}$, it is more prominent that the rate of grain growth at certain locations on the molybdenum coating surface exceeds that at other ones, resulting in preferential grain growth at these growth points, thus producing coarse grains. In addition, relatively rapid grain growth is accompanied by nucleation, resulting in voids on the surface, which reduces the flatness [27,28].

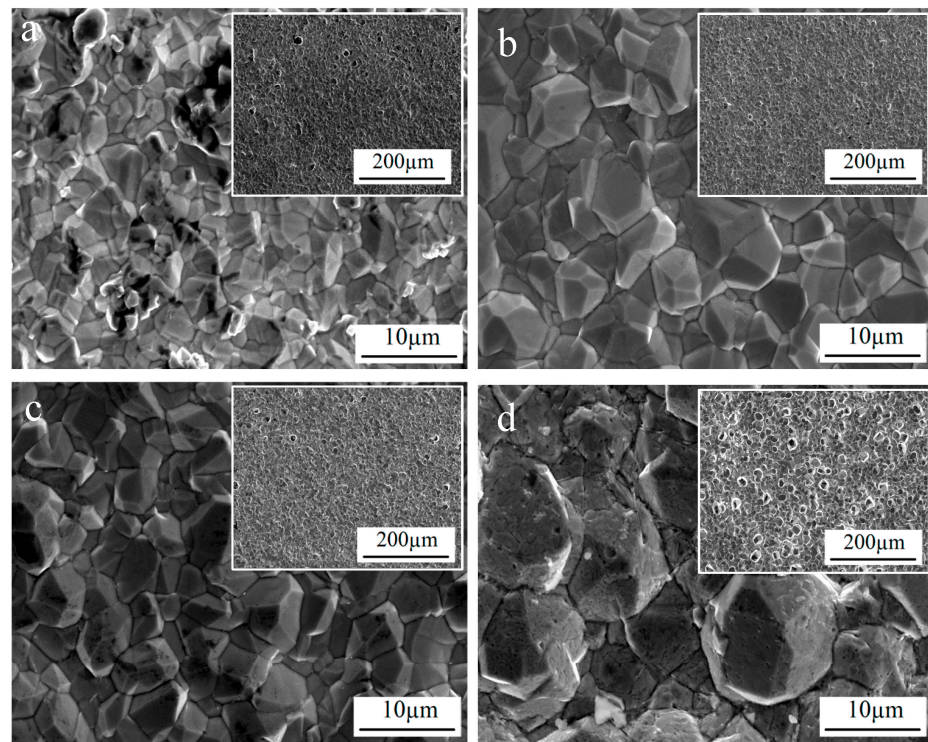


Figure 3. SEM images of the surface morphology of molybdenum coatings prepared by electrodeposition in $\text{Na}_3\text{AlF}_6\text{-NaF-Al}_2\text{O}_3\text{-MoO}_3$ system at 930°C for 60 min at different current densities ((a). $10\text{ mA}\cdot\text{cm}^{-2}$; (b). $30\text{ mA}\cdot\text{cm}^{-2}$; (c). $50\text{ mA}\cdot\text{cm}^{-2}$; (d). $70\text{ mA}\cdot\text{cm}^{-2}$).

Subsequently, the cross-sectional morphologies of molybdenum coatings at different current densities were characterized by SEM, as shown in Figure 4.

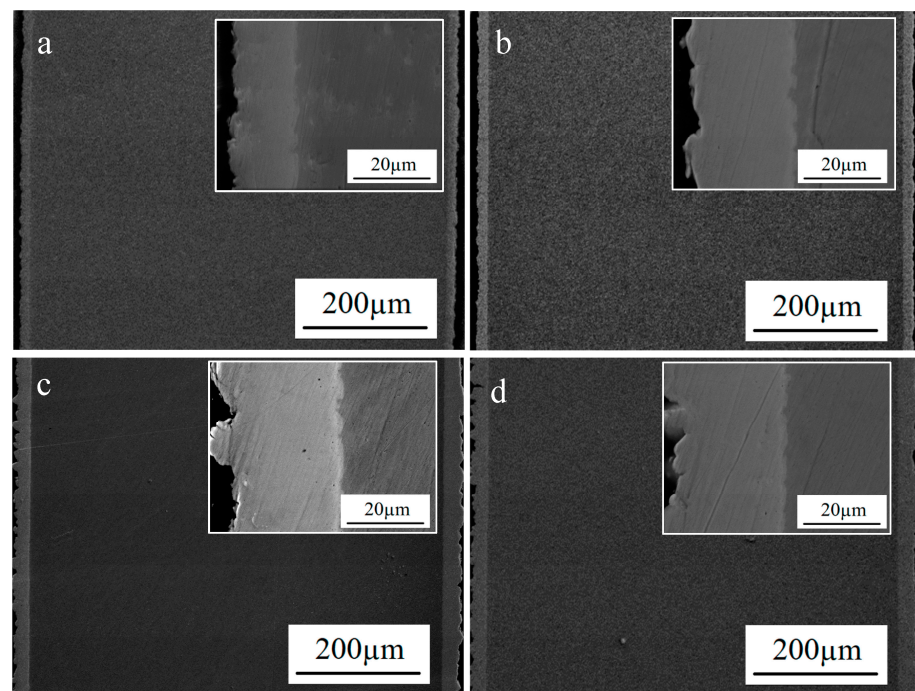


Figure 4. SEM images of cross sections of molybdenum coatings prepared by electrodeposition in $\text{Na}_3\text{AlF}_6\text{-NaF-Al}_2\text{O}_3\text{-MoO}_3$ system at 930°C for 60 min at different current densities ((a). $10\text{ mA}\cdot\text{cm}^{-2}$; (b). $30\text{ mA}\cdot\text{cm}^{-2}$; (c). $50\text{ mA}\cdot\text{cm}^{-2}$; (d). $70\text{ mA}\cdot\text{cm}^{-2}$).

From Figure 4, it can be seen that the molybdenum coatings prepared at different current densities were dense and tightly bonded to the nickel substrate. In addition, the thickness of the molybdenum coatings on the front and back sides of the nickel substrate was nearly the same. When the current density was 10 and 30 $\text{mA}\cdot\text{cm}^{-2}$, the molybdenum coating was dense and relatively flat with a thickness of 10 μm and 20 μm , respectively, free of cracks. As the current density increased to 50 and 70 $\text{mA}\cdot\text{cm}^{-2}$, the thickness of the molybdenum coating increased to 26 μm and 30 μm , respectively. The surface flatness of the molybdenum coating decreases, exhibiting an obviously hilly structure, mainly because the molybdenum atoms produced by electrodeposition grow preferentially on the protrusions of the grains when the current density increases, which makes the coating thickness at different locations not as uniform as that at low current densities [29]. These results agree with that of the dependence of the surface morphology of the molybdenum coating on the current density shown in Figure 3.

In summary, the prepared molybdenum coatings on nickel substrates were dense and coherent when the current density was between 10 and 70 $\text{mA}\cdot\text{cm}^{-2}$. The cathodic current efficiencies for preparation of them under these current densities were calculated to be above 97%. This indicates that the current density in this range almost has no impact on the current efficiency.

It has been reported that in KF-based molten salts for electroplating of molybdenum coating [20,23], as shown in Table 1, the cathode current efficiency was dramatically reduced to below 80% at a current density of around 70 $\text{mA}\cdot\text{cm}^{-2}$ due to the formation of dendrites and black powder. In the present investigation, when the current density was at 70 $\text{mA}\cdot\text{cm}^{-2}$, the current efficiency was similar to that under 10–50 $\text{mA}\cdot\text{cm}^{-2}$, which was above 97%. Therefore, it is assumed that the employment of higher current density might be available for producing molybdenum coatings in Na_3AlF_6 -NaF- Al_2O_3 - MoO_3 system with an acceptable coating quality and current efficiency.

Table 1. Comparison of different systems for electrodeposition of molybdenum.

System	Current Density ($\text{mA}\cdot\text{cm}^{-2}$)	Cathode Current Efficiency (%)	Visual Evaluation
KF (85 mol %)- K_2MoO_4 (10 mol %)- SiO_2 (5 mol %) [20]	7.3	98.3	Smooth deposit
	15.6	98.5	Smooth deposit
	29.3	92.5	Smooth deposit
	44	90.6	Smooth deposit, dendrites
	63.3	77	Smooth deposit, Black powder
	87.9	24.8	Black powder
	146.6	24.5	Black powder
KF- MoO_3 (95:5 mol %) [23]	11	92.5	Smooth deposit
	33	91	Smooth deposit
	55	79	Smooth deposit
	77	73	Smooth deposit, dendrites
Na_3AlF_6 -NaF (21:79 mol %)- Al_2O_3 (0.015 mol %)- MoO_3 (5 mol %)	10	97	Smooth deposit
	30	97	Smooth deposit
	50	97	Smooth deposit
	70	97	Smooth deposit

3.2. Effect of Electrodeposition Time on Molybdenum Coating

The effects of different electrodeposition times on the surface morphology of molybdenum coatings at a current density of 30 $\text{mA}\cdot\text{cm}^{-2}$ in the Na_3AlF_6 -NaF- Al_2O_3 - MoO_3 system were investigated at 930 °C. The SEM images are shown in Figure 5.

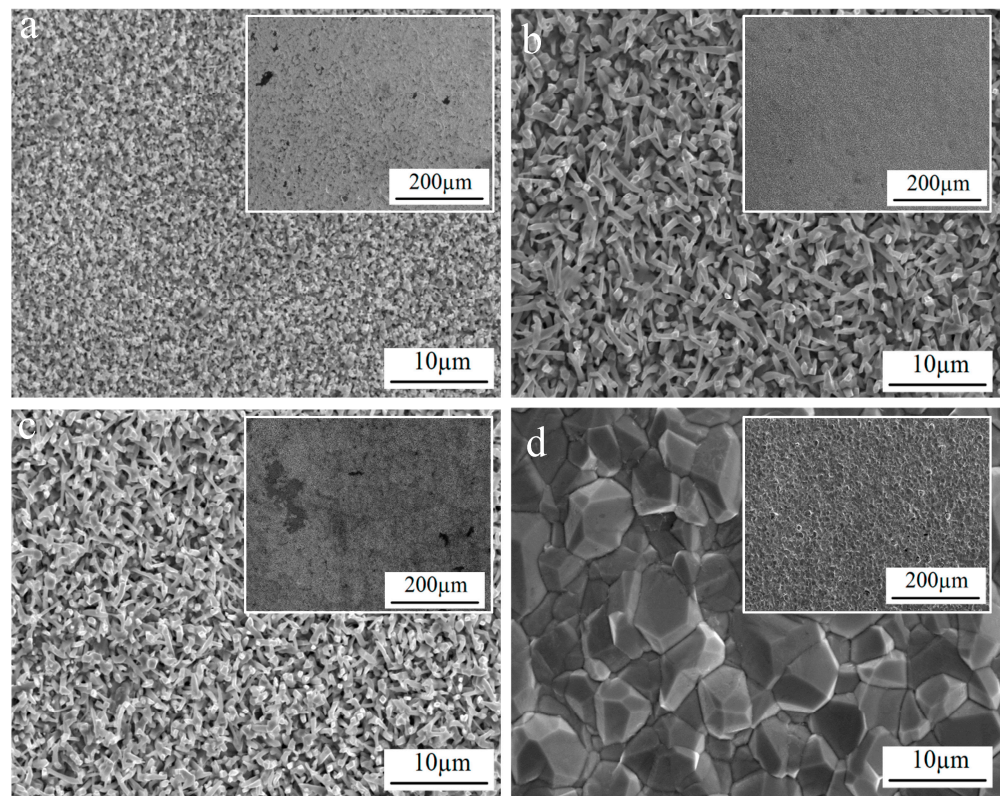


Figure 5. SEM images of the surface morphology of molybdenum coating prepared by different electrodeposition times in $\text{Na}_3\text{AlF}_6\text{-NaF-Al}_2\text{O}_3\text{-MoO}_3$ system at 930°C with a current density of $30\text{ mA}\cdot\text{cm}^{-2}$ ((a). 10 min; (b). 20 min; (c). 30 min; (d). 60 min).

When the electrodeposition time was 10 min, some parts of the nickel substrate surface were not covered by molybdenum. The molybdenum grains were fine, and there were still gaps between the grains. When the electrodeposition time was 20 min and 30 min, the molybdenum coating almost covered the whole nickel substrate surface, and the molybdenum grain size became larger, with a fibrous morphology. As the electrodeposition time was increased to 60 min, the molybdenum coating completely covered the nickel substrate. The surface was compact and consisted of well-developed polyhedral molybdenum grains with larger sizes.

The growth of electrodeposited coatings is an electrochemical crystallization process. At the beginning of electrodeposition, nuclei are generated, and the rate of nuclei generation is faster than that of grain growth, resulting in fine and loose grains being observed on the coating surface. Increasing the electrodeposition time, the grain growth rate is gradually accelerated, and the grain size becomes larger, but it is not enough to fill all the inter-grain gaps. As the electrodeposition time is further increased, the grain growth rate is higher than the nuclei generation rate, which makes the grains fully grow up. As a result, the inter-grain gaps disappear and the polyhedral crystals are well developed, forming a dense coating [30].

Compared with the electroplating of molybdenum coating in a molten KF-MoO_3 system [23], it is found that the molybdenum grains obtained in the early stage of electrodeposition in the present molten system are very small in size, the nucleation rate is more rapid and the grain growth rate is slower, so the number of crystals is high. At a similar current density of around $30\text{ mA}\cdot\text{cm}^{-2}$ under the electroplating for the same duration of 60 min, in the present investigation molybdenum coatings with more uniform distribution of grain size could be produced than that in KF-MoO_3 melt. This makes it possible to produce a dense molybdenum coating even with longer electrodeposition time (i.e., more than 60 min) in $\text{Na}_3\text{AlF}_6\text{-NaF-Al}_2\text{O}_3\text{-MoO}_3$ molten salts.

3.3. Preparation of Thick Molybdenum Coating

Based on the above results and discussion, it is assumed that it could be possible to increase the current density and electrodeposition time to produce molybdenum coatings with increased thickness in a molten $\text{Na}_3\text{AlF}_6\text{-NaF-Al}_2\text{O}_3\text{-MoO}_3$ system. Therefore, electrodeposition was carried out at a current density of $100\text{ mA}\cdot\text{cm}^{-2}$ for 3 h at $930\text{ }^\circ\text{C}$ to prepare thick molybdenum coatings on a nickel sheet and wire, respectively, and the corresponding photographs and SEM images of the deposits are presented in Figure 6.

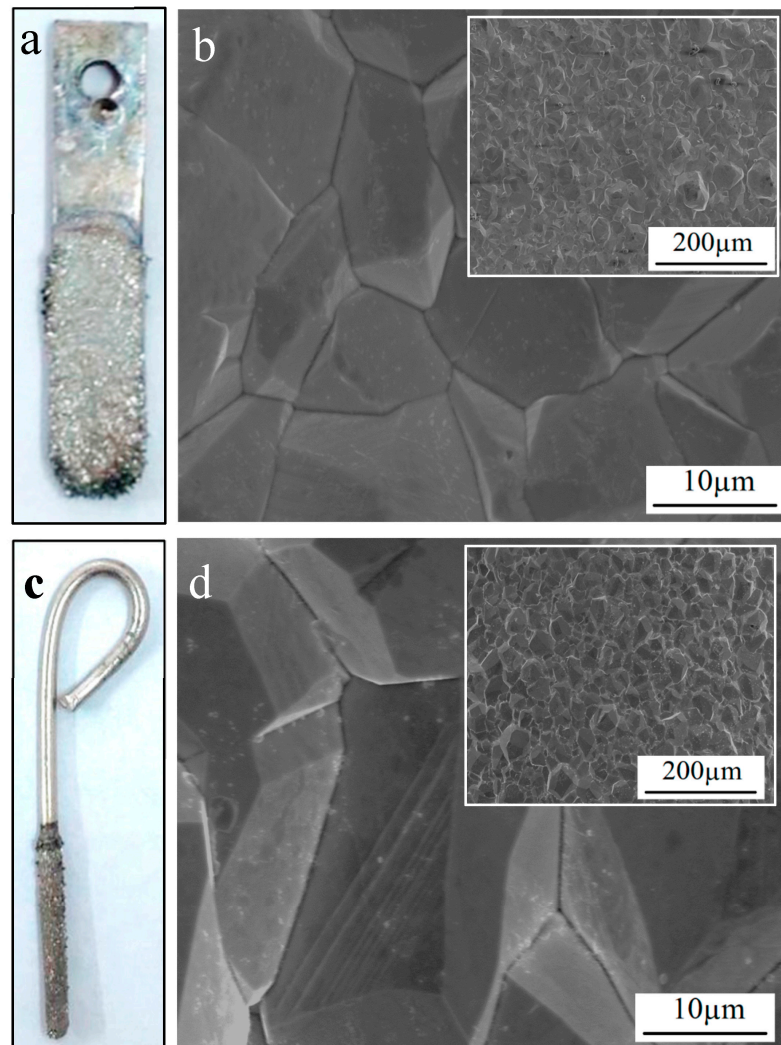


Figure 6. Appearance and SEM images of molybdenum coating prepared by electrodeposition in $\text{Na}_3\text{AlF}_6\text{-NaF-Al}_2\text{O}_3\text{-MoO}_3$ system at a current density of $100\text{ mA}\cdot\text{cm}^{-2}$ for 3 h at $930\text{ }^\circ\text{C}$ ((a,b). nickel sheet; (c,d). nickel wire).

Figure 6a,c shows the photographs of molybdenum coating deposited on a nickel sheet and wire, respectively, demonstrating a distinct metallic luster. Typical SEM observation of them, as demonstrated in Figure 6b,d, revealed that both surfaces were dense and relatively flat, with relatively uniform grain size distribution.

Figure 7 demonstrates the cross-section of the electroplated molybdenum coating on the nickel sheet and wire. It can be seen that they were relatively flat, uniform, and dense, with good adhesion to the nickel substrate. Their thicknesses were 125 and $140\text{ }\mu\text{m}$, respectively, and there was no significant difference between the thicknesses on the front and back sides for nickel sheets. The cathodic current efficiency was calculated to be 79.8% and 85.9%, respectively.

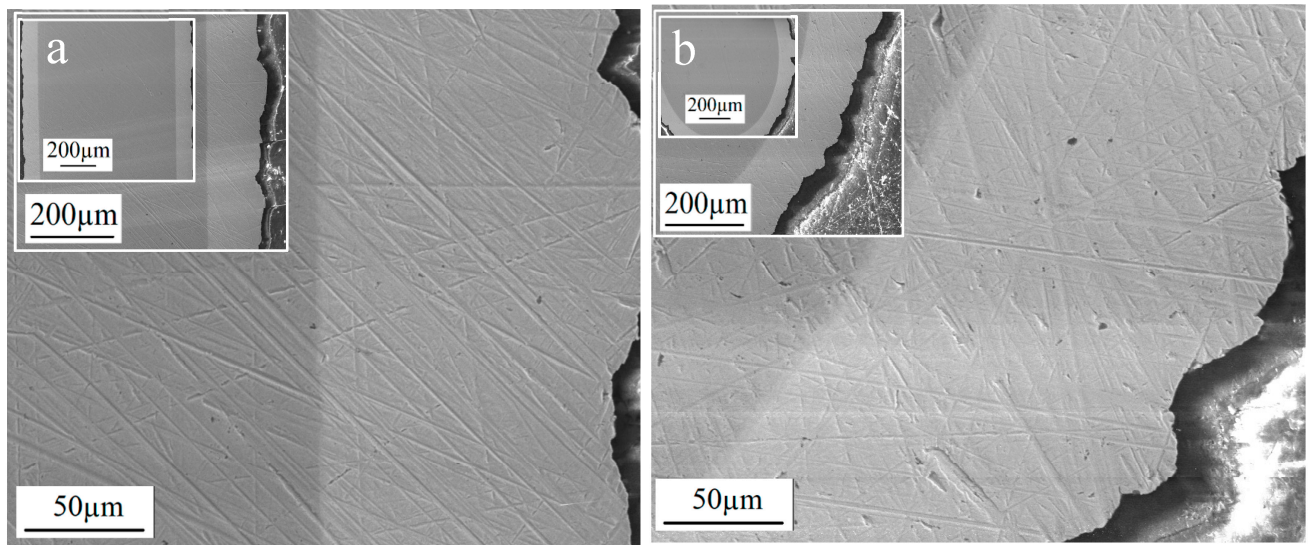


Figure 7. Cross-sectional SEM images of molybdenum coatings prepared by electrodeposition in $\text{Na}_3\text{AlF}_6\text{-NaF-Al}_2\text{O}_3\text{-MoO}_3$ system at a current density of $100 \text{ mA}\cdot\text{cm}^{-2}$ for 3 h at 930°C ((a). nickel sheet; (b). nickel wire; top-left insets, low and middle magnification images).

Furthermore, the electroplating of thick molybdenum coating under a higher current density ($300 \text{ mA}\cdot\text{cm}^{-2}$) was carried out in $\text{Na}_3\text{AlF}_6\text{-NaF-Al}_2\text{O}_3\text{-MoO}_3$ melt for 1 h at 930°C . The SEM images of the surface and cross-section of the produced coating are presented in Figure 8.

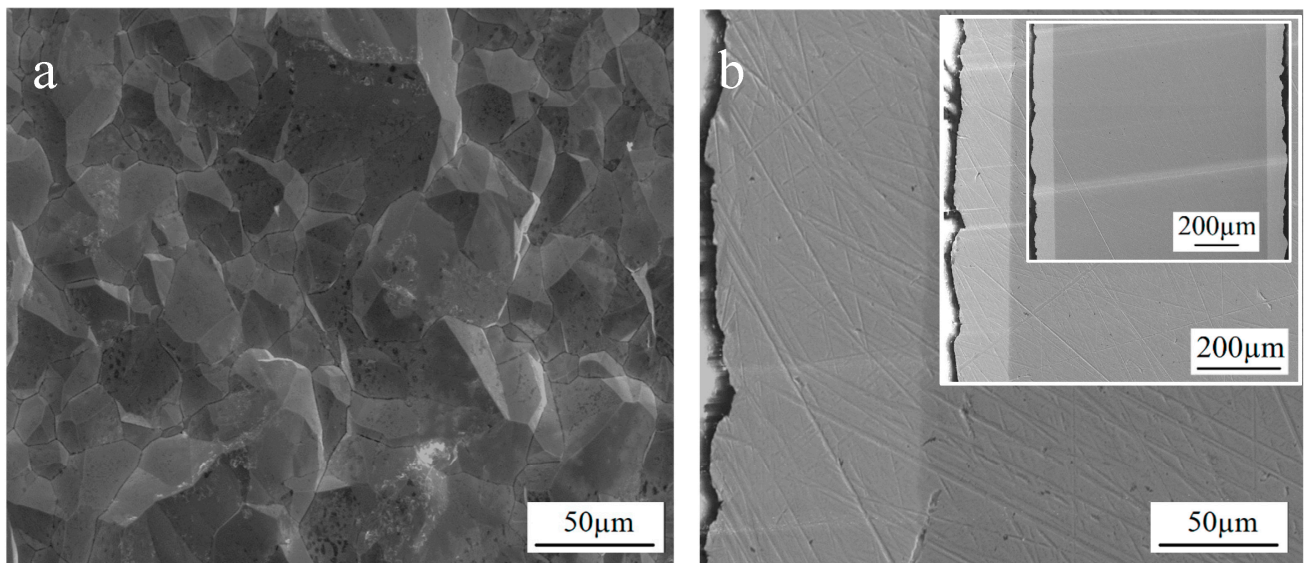


Figure 8. SEM images of the surface (a) and cross-section (b) of molybdenum coating prepared by electrodeposition at a current density of $300 \text{ mA}\cdot\text{cm}^{-2}$ for 1 h in $\text{Na}_3\text{AlF}_6\text{-NaF-Al}_2\text{O}_3\text{-MoO}_3$ system at 930°C .

As shown in Figure 8a, the surface of the molybdenum coating was dense with coarser grains. In Figure 8b, the coating was dense and closely bonded with the substrate with a thickness of $100 \mu\text{m}$. And the cathode current efficiency of the electrodeposition process was calculated as 72.4%, which is lower than that at $100 \text{ mA}\cdot\text{cm}^{-2}$ for 3 h. This may be due to the possible formation of dendrites, ascribed to more serious concentration polarization at such high cathode current density.

Therefore, in the $\text{Na}_3\text{AlF}_6\text{-NaF-Al}_2\text{O}_3\text{-MoO}_3$ system, it is suggested that at a current density of less than $100 \text{ mA}\cdot\text{cm}^{-2}$, a dense, coherent, and adhesive molybdenum coating with a larger thickness (more than $150 \mu\text{m}$) could be produced with longer electrodeposition duration under an acceptable cathode current efficiency.

4. Conclusions

The electrodeposition of molybdenum coatings was carried out in a $\text{Na}_3\text{AlF}_6\text{-NaF-Al}_2\text{O}_3\text{-MoO}_3$ molten salt system at 930°C at different current densities and electrodeposition times. Dense, coherent, and relatively flat molybdenum coatings were prepared on nickel substrates. With the increase of current density ($10\sim 70 \text{ mA}\cdot\text{cm}^{-2}$), the thickness of the molybdenum coating was increased from $10 \mu\text{m}$ to $30 \mu\text{m}$. Under all the current densities, the coatings were compact and coherent, with a current efficiency of more than 97%.

At a current density of $30 \text{ mA}\cdot\text{cm}^{-2}$, with the increase of electrodeposition time ($10\sim 60 \text{ min}$), it was found that at the initial stage of electrodeposition, the formation of a large amount of fine molybdenum crystals results in maintaining relatively small crystals even at 60 min, ensuring the flatness and uniformity of the produced coating. The morphology of the deposits changed from fine, fibrous to well-developed faceted crystals.

Molybdenum coatings with a thickness of $125 \mu\text{m}$ and $140 \mu\text{m}$ were obtained on a nickel sheet and wire, respectively, at a current density of $100 \text{ mA}\cdot\text{cm}^{-2}$ for 3 h of electrodeposition. The current efficiency was calculated to be 79.8% and 85.9%. The coatings were dense, uniform, and relatively flat. At a current density of $300 \text{ mA}\cdot\text{cm}^{-2}$, a thick and dense molybdenum coating was also obtained by electrodeposition for 1 h, with a lower current efficiency of 72.4%.

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