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Research on Protective Coating on Inner Surface of Alloy Tube

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Abstract. Materials are one of the most important factors which limit reactor development. Molten salt not only used as the coolant but used as application in which fissile materials and fission products are dissolved in Molten Salt Reactors (MSRs). Therefore the corrosion resistance of structure materials is the one of most important aspects for application in MSRs. Compatibility and chemical stability with the molten salt should be considered for some common structural alloys such as Incoloy-800H. In this research, the pure nickel coating was obtained by electroplating on the inner surface of nickel alloy to improve the corrosion resistance. However, there are some problems for plating on the inner surface of tube. For example the current is shielded and the anode is easy to passivate. The inner anode was used for solving these problems in this study. Pure nickel coating was obtain and the microstructure and properties of coating were analysed using this method. The thickness, hardness and microstructure of coating were observed by metallographic microscope, micro hardness tester and field emission scanning electron microscope, and the influence of deposition duration and annealing treatment duration on properties were analysed. Thermal shock performance was investigated as well. The results showed that the coating thickness increased linearly with the increasing of plating durations and the size of grain increased with the durations as well, the surface of coating became inhomogeneous correspondingly. The hardness of coating changed as the change of durations of annealing treatment. The thermal shock test showed that bonding strength of coating with substrate was good.

1. Introduction

Nuclear energy is recognized as a safe, economical and low-carbon energy source all over the world. It is also the best choice to solve the problems of low-carbon economy, emission reduction and environmental stress [1]. After the Fukushima Daiichi nuclear accident, the safety of nuclear power and nuclear power plant how to deal with sudden natural disasters have caused widespread concern [2], meanwhile, researchers accelerated the pace of research on higher security nuclear power technology. Molten salt reactor (MSR) has become one of research hot spots because of its characteristics such as high inherent safety and recyclability of nuclear fuel. However, materials corrosion has been recognized as an issue in molten salts [3]. According to Fabre et al. [4], the corrosion rates of Ni, Mo and W were smaller than that of Fe in LiF-NaF. The corrosion performance of a number of nickel-based alloys in molten FLiNaK salt at 850 ℃ was study by Olson [5], the results showed that the Ni-201 alloy, which did not contain Cr, was resistant to corrosion, and the corrosion weight loss of Cr-

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content alloy correlated with the Cr-content of the corresponding alloy. At present, nickel-base alloy with good high-temperature resistance is studied for structural material of MSR, but the corrosion resistance of molten salt is not ideal, because most of them contain Cr, Fe and other elements. According to common alloying constituents to corrode in molten salts increased in the following order [6]: Ni, Co, Fe, Cr, Al, we can see that it can be increased the nickel-based alloy corrosion resistance in molten salts to obtain a layer of pure nickel on the alloy matrix [7].

Pulse electroplating is an effective technology for obtaining high properties coating, this process involves the swift alternating of the voltage or current between two different values resulting in a series of pulses of equal amplitude, duration and polarity, separated by zero current. By changing the pulse amplitude and width, it is probable to change the deposited film's composition and thickness [8]. A large number of experiments showed that pulse electroplating is better than direct electroplating. The deposition layer obtained by pulse electroplating is uniform and compact, and the corrosion resistance of the layer is better than the layer obtained by dc method. In addition, the layer has a lower porosities, higher brightness and conductivity using pc method [9,10]. Y H Liu et al.[11] used different plating solutions to prepare nickel coatings on plate substrates, it was found that the nickel coating prepared by the nickel sulfamate system had better performance. The effects of duty ratio on the corrosion resistance of nickel coating prepared on cooper substrate in NaCl solution was studied by L Zhou et al. [12], who found that the smaller duty ratio, the better brightness and corrosion resistance coating was obtained. The similar research reported by Sivasakthi P et al. [13], they found that the micro-hardness of nickel coating increased with the duty ratio and pulse frequency decreased.

Most of corrosion resistant structural materials are used in pipeline system of MSR, the studies of nickel coating on the surface of tubular substrate prepared by electroplating are rarely reported. At present, there are some technical difficulties in electroplating coating on the inner surface of tubular substrate. If the anode is arranged in the outside of tube, the current in tube will be blocked, and this will result in obstacles to plating coating on the inner surface of tube; if the anode is placed inside the tube, the area ratio of cathode to anode is large, the current density of anode will be far more than the cathode, it will result in anodic passivation. To solve these problems, the experimental apparatus was designed and the electroplating time was controlled respectively, the nickel rod with diameter of 4 mm and length of 95 mm was used as the internal anode, the 800H nickel-base alloy tube with diameter of 25 mm and length of 50 mm was used as substrate, and the nickel coating on inner surface of tube was prepared by pulse electroplating. In this study, the thickness, hardness and surface morphology of coating were observed respectively, and the thermal shock test was carried out simultaneously.

2. Experimental

2.1. Electroplating solution preparation

Sulfamate solution was used in this research, and table 1 shows the composition of electroplating solution. The solution of nickel sulfamate, boric acid and nickel chloride were configured respectively, then mixed the three solutions and adjusted the pH to acidic, finally added sodium dodecyl sulfonate in the solution, and mixed well.

Table 1. The composition of electroplating solution

Composition	Concentration (g·L^{-1})
$Ni(NH_2SO_3)_2 \cdot 4H_2O$	400~500
H_3BO_3	30~40
$NiCl_2 \cdot 6H_2O$	10~20
$C_{12}H_{25}SO_3Na$	0.05~0.15

2.2. Sample pretreatment

The anode was a nickel rod with purity of 99.9%, and the cathode was a nickel-based alloy tube, the anode and cathode were pretreatment to remove surface defects, impurity and oxide film. The process

of pretreatment was as follows: sandpaper grinding → washing → alcohol degreasing → washing → chemical degreasing → washing → pickling → washing → activation → washing →drying.

2.3. Experimental procedure

Figure 1 below shows the experimental apparatus. The anode and cathode were fixed on the pendant and placed in the solution, the cathode. The position of anode and cathode was adjusted respectively to ensure that the anode was in the center of nickel-based alloy tube and the cathode was put completely into the solution. Finally the wires were connected to the pulse power. According to previous work [11, 12, 14, 15], the parameters were set as shown in table 2 below. After electroplating, the tube was taken out and washed by ultrasonic cleaning, then annealed at 500 ℃ for 2 h, 4 h and 6 h respectively. Afterwards, the sample was cut into rings shape with thickness of 1 cm, and rectangular shape along the axial direction of the tube. The thickness, hardness and microstructure of the coating were investigated. In addition, the thermal shock test was investigated using the ring samples. The parameters of test as follows: 500 ℃ for 5 min followed by quenching. The pulse power supply used in this experiment was HP-MCC, and the SX-G08133 muffle furnace was used for annealing treatment and thermal shock test. The hardness of the samples was tested by HMV-G21 microhardness tester, the loading was 980.7 mN holding for 10 s. The thickness of coating was observed using a DMILM inverted metallographic microscope. The surface morphology of coating was observed by JSM-7001F field emission scanning electron microscopy (FESEM), and the elemental characterization was carried out using energy dispersive spectrometer (EDS).

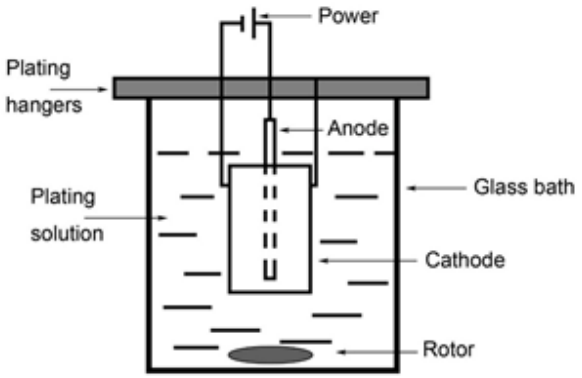


Figure 1. Diagram of experimental apparatus

Table 2. Experiment parameters

Experiment parameter	Value
Current density ($A \cdot dm^{-2}$)	3
Duty factor	20%
Cycle (ms)	10
Temperature (℃)	50
Duration of deposition *t* [h]	1-3

3. Results and discussion

3.1. Effect of electroplating duration on the thickness of coating

Thickness is an important index of the quality for coating. For molten salt reactor protective coating, in order to ensure the effect of protection, thickness should be more than 40 μm [16]. Electroplating duration is the most important parameter when others are fixed. Figure 2 shows the thickness of the coating in different electroplating durations. When the electroplating durations were 1 h, 1.5 h, 2 h,

and 3 h respectively, the thickness of coatings was 32.8 μm, 42.0 μm, 75.0 μm and 138.4 μm accordingly. Figure 3 (a) displays the relationship between the thickness of coating and electroplating duration. It can be seen from graph, the thickness of coating increases with the extension of electroplating duration, and the change is an approximately linear relation. The following formula for the relationship between the thickness and duration was used in Ref. [17]

$$d = \frac{J_k \eta_k K t}{1000 \rho} \tag{1}$$

where d is thickness of coating (mm)； J_k is cathode current density ($A \cdot dm^{-2}$), η_k is current efficiency, K is electrochemical equivalent [$g \cdot (A \cdot h)^{-1}$)] t is electroplating duration (h), and ρ is density of coating ($g \cdot cm^{-3}$)

In this research, J_k was fixed, and K and ρ were constant value for electroplating nickel, η_k was generally between 85% and 100%. Therefore, according to formula (1), d was a linear function of t, and the result of this study conformed to this law. Due to the occurrence of side reactions such as hydrogen evolution during the process of electroplating and stirring in the tube was weakened, the current efficiency may be unstable and the growth rate of the coating may be affected. In addition, when the electroplating duration was controlled within 3 h, the current efficiency was not reduced, indicating that the anode was not passivated at this time.

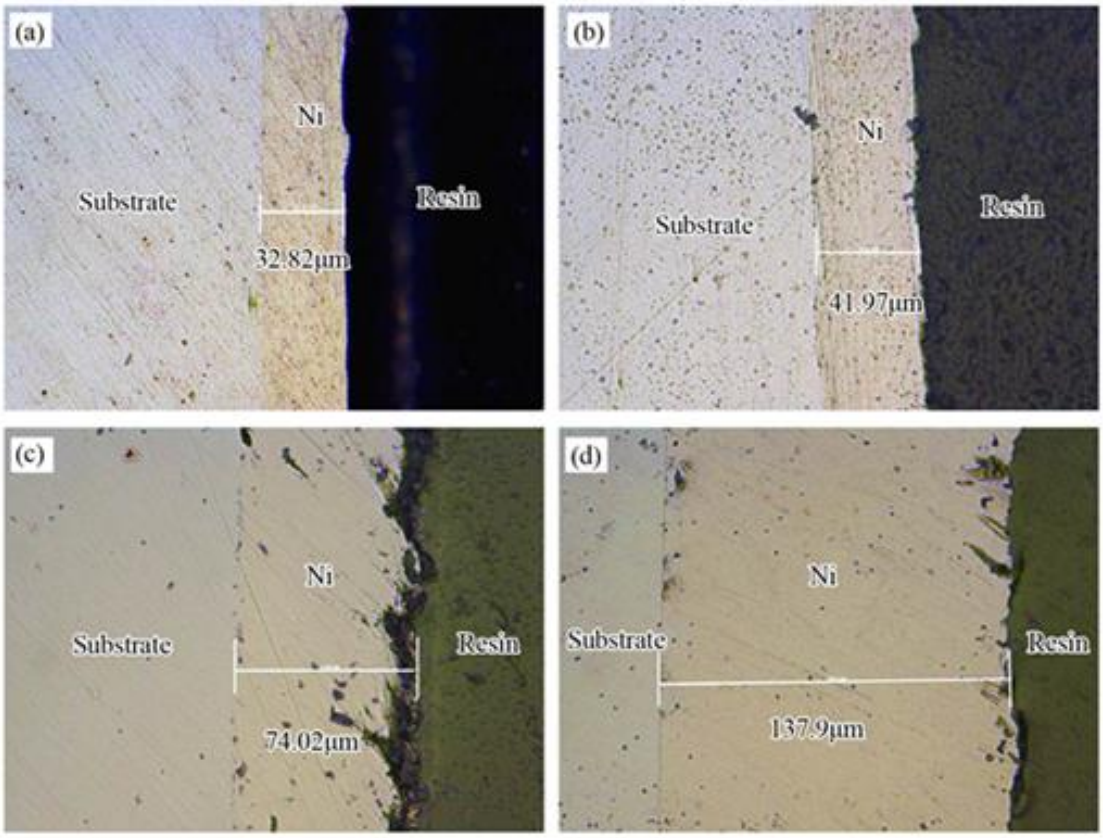


Figure 2. Thickness of coating in different electroplating duration

(a) 1 h; (b) 1.5 h; (c) 2 h; (d) 3 h

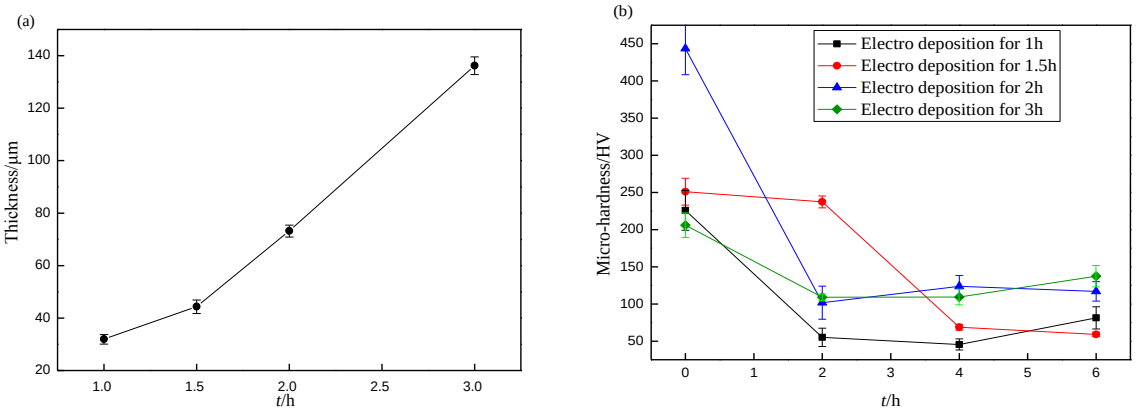


Figure 3. (a) Curve of thickness with electroplating duration; (b) Curves of coating hardness with annealing treatment duration

3.2. Effect of annealing time on hardness of coating

Figure 3 (b) shows the curve of Vickers hardness of coating with the annealing time, and it also shows the effect of different electroplating duration on the hardness of coating. Without annealing, the hardness of coating increased first and then decreased with the extension of the electroplating duration, when the duration was 3 h, the hardness of coating was minimum and was 206 HV; when the duration was 2 h, the hardness was maximum and was about 443 HV. The most probable explanation of this phenomenon is that the structure of coating prepared by 2 h was more compact and uniform, another reason might be that the high hardness of nickel alloy substrate (the hardness of nickel alloy greater than that of pure nickel hardness), and the decreasing influence of the alloy substrate on the coating as the coating thickness increase. Moreover there might be more carbon, silicon and other elements or some impurity ions in coating for 2 h, which caused the increase of hardness. When the annealing treatment duration was 2 h, the hardness of coating prepared at the different time was obviously decreased, except the coating prepared by 1.5 h, and the hardness increased with the extension of annealing treatment duration, but the change was not obvious. After 6 h annealing treatment, the final hardness were 81 HV, 59 HV, 117 HV and 137 HV respectively. The study by Luo Y et al. [18] showed that the recovery and recrystallization of coating would occur above 450 °C, it caused residual stress of coating release. Therefore the hardness would decrease after annealing treatment. With the prolongation of annealing treatment duration, the change of hardness was not obvious. The hardness of Ni-based alloy substrate before annealing was 335 HV and 312 HV after that, which indicated that the coating had no effect on the mechanical properties of substrate.

3.3. Surface morphology

The surface morphology of coating after 2 h annealing treatment was observed by SEM and the coating samples of different deposition durations were compared and analyzed. Figure 4 (a) and (b) show that the coatings are both uniform and compact, but the surface of coating electrodeposited for 1 h has slight scratches, it was probable that the growth of the coating tended to the surface structure of substrate after grinding. While, there are still some holes on the surface plating for 1.5 h, which may be due to hydrogen evolution reaction on the surface of cathode during electroplating, as hydrogen vesicles were electrical insulators, nickel ions cannot penetrate the bubble to discharge, resulting in the partial area of coating without nickel deposition, forming holes. From figure 4 (c) and (d), it can be seen that the grains are obvious, and the surface is not smooth. The grains of coating electrodeposited for 2 h are fine and uniform, the size of grain between 0.5 μm and 2 μm, and the grain boundaries are obvious, while, the grains of coating deposited for 3 h become coarse and the size becomes non-uniform, which means that the grain size of coating increased gradually with prolongation of

electroplating duration. This can probably be explained by considering that the atoms were preferentially deposited at the tip of the large particles with the extension of electroplating duration, then the large particles grew up and the surface of coating gradually became rough.

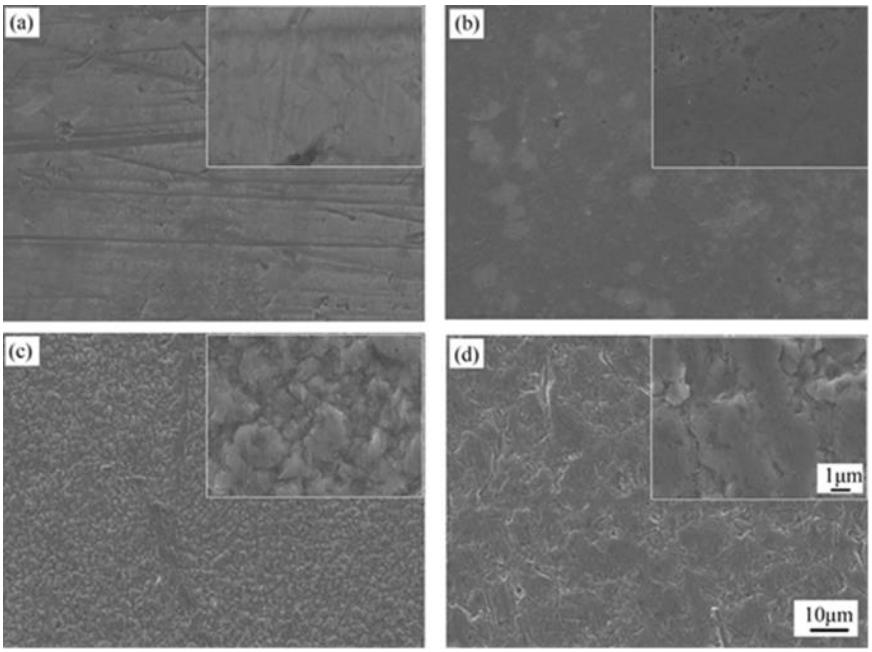


Figure 4. Microscopic morphology of coatings at different deposition duration

(a) 1 h;(b) 1.5 h; (c) 2 h; (d) 3 h

3.4. Thermal shock test

The thermal shock was investigated to reveal the ability of coating to withstand thermal stress in our research. After annealing, the sample was cut into rings with thickness of 1 cm, and then subjected to a cycle test at 500 ℃ for 5 min followed by quenching. After 20 cycles, surface of coating did not appear crack, blister, peeling and so on, but there was a slight partial oxidation, it is indicated that the ability of coating to withstand thermal stress was good, and coating had high bonding strength with inner surface of tube. Figure 5 shows the appearance of sample without thermal shock test (left side) and after 20 cycles of thermal shock (right side). In addition, the cross section of sample after thermal shock was observed by SEM. As shown in figure 6, there is no cracking at the boundary between coating and substrate; EDS analysis shows that there is no obvious oxygen peak appeared in the EDS pattern. The results show that coating is not oxidized, and there is nickel enrichment on the substrate near the boundary, the probably reason might be that nickel ions migrate to substrate during annealing. In addition, the peak of carbon, silicon and other elements in coating may also be atomic diffusion during annealing treatment.



Figure 5. Photo of sample without thermal shock test and after 20 cycles of thermal shock
(a) without thermal shock test; (b) after 20 cycles of thermal shock

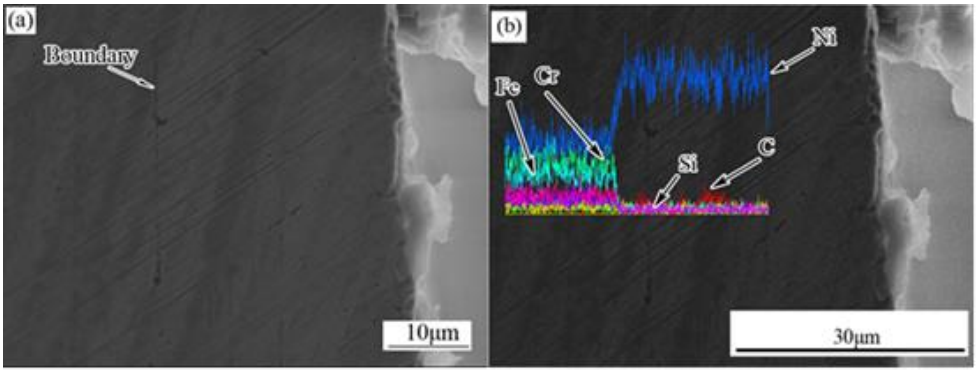


Figure 6. The SEM image and EDS analysis of cross section of coating after 20 cycles of thermal shock test
(a) SEM image; (b) EDS analysis

4. Conclusions

Pure nickel coating was successfully electrodeposited using internal anode on the inner surface of tubular substrate, and the quality of coating can be controlled by electroplating parameters and post-treatment. The thickness, surface morphology and hardness of coating can be controlled by electroplating duration and annealing treatment respectively. The coating has good bonding strength with tube shape substrate, and good oxidation resistance. The results of this study provide some necessary data for the research of the protective coating on pipeline in MSR.

5. References

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