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Dynamic Parameters of Jet Electrodeposition for Ni-P Alloy†

Y. WANG[1], M. KANG[1,2,*], S.W. JIN[1] and X.Q. FU[1]

[1]College of Engineering, Nanjing Agricultural University, Nanjing 210031, P.R. China
[2]Jiangsu Key Laboratory for Intelligent Agricultural Equipment, Nanjing 210031, P.R. China

*Corresponding author: Fax: +86 25 58606699; Tel: +86 25 58606667; E-mail: kangmin@njau.edu.cn

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To study the electrochemical dynamic law in the process of jet electrodeposition for Ni-P alloy, the coating was prepared with self-developed device on the 45 carbon steel substrate. The influence of process parameters including the electrolyte temperature, dipolar space and electrolyte flow velocity on the dynamic parameters was examined by the potential sweep method. The experimental results show that within the range of experiments, the electrolyte temperature had small impact on the reversibility of the system, while the polarization resistance decreased with the increasing electrolyte temperature. The dipolar space had little effect on the reversibility of the system and the polarization resistance first decreased and then increased with the increase of dipolar space. The electrolyte flow velocity displayed the greatest impact on the reversibility of the system, meanwhile the polarization resistance increased with the increase of electrolyte flow velocity.

Keywords: Jet electrodeposition, Ni-P alloy, Process parameters, Dynamic parameters.

INTRODUCTION

Nickel-phosphorus (Ni-P) alloy coatings, with their high wear resistance, corrosion resistance and hardness, have played an important role in extending the service life and reliability of engineering components, as well as in boosting the performance and quality of mechanical equipment. However, the Ni-P alloy prepared by traditional electrodeposition with low limit current densities has relatively slow deposition rate and low production efficiency, therefore cannot satisfy the need of modern production[1,2]. Jet electrodeposition, which has been developed in recent years, may significantly increase the deposition rate because it can accelerate the transfer process of electrodeposition material, augment the maximum current density and improve the cathodic polarization effects[3]. Changing the parameters of jet electrodeposition would alter the deposition rate and coating quality. Studying electrochemical kinetics can help people figure out how to control reaction conditions[3] and to improve the reaction speed and production efficiency. So far, most of the studies on kinetics have focused on the electroless coating of Cu, Ni-B alloy and Co-B alloy[4,5]. There are few researches concerning the rate of deposition of Ni-P alloy. Although there are some studies on the effects of process parameters on rate of deposition Ni-P alloy, the kinetics of electrode process and dynamic parameters in the process of jet electrodeposition for Ni-P alloy haven't been reported. On the other hand, a lot of machinery parts are made of 45 carbon steel whose performance is poor. In this work, the Ni-P alloy coating was produced by jet electrodeposition on the 45 carbon steel substrate and the influence of process parameters including the electrolyte temperature, dipolar space and electrolyte flow velocity on dynamic parameters was investigated using the potential sweep method.

EXPERIMENTAL

Jet electrodeposition: Experimental equipment of jet electrodeposition was self-developed and composed of thermostatically controlled plating bath, circulatory system of plating solution and electrochemical measurement system. The electrolyte was jetted on the workpiece through the anode nozzle with the action of a strong electric field, thereby the electrodeposition was realized as shown schematically in Fig. 1. By using this equipment, the deposition rate was increased greatly and the production efficiency was improved significantly. As the substrate surface cleaning is extremely important, the substrate was subjected to a series of conventional pretreatment procedures before plating. Reagents with analytical quality and doubly distilled water were used to prepare the plating solution. The electroplating components are listed in Table-1.

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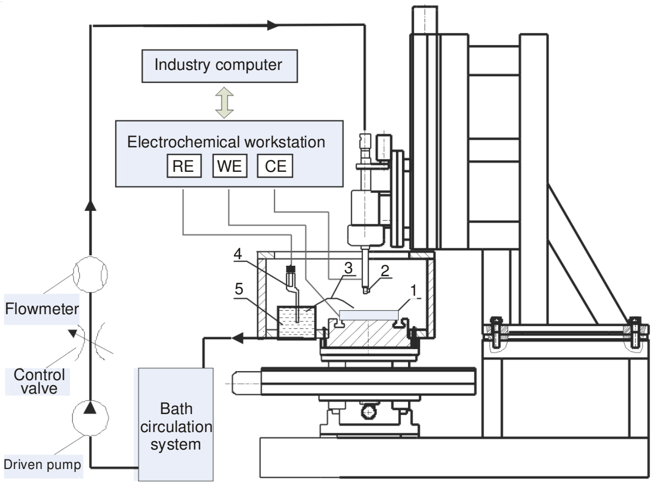

Fig. 1. Diagram of experimental equipment for jet electrodeposition 1. Workpiece 2. Anode nozzle 3. Lugging capillary 4. Reference electrode 5. Salt bridge. Note: WE is working electrode; RE is reference electrode; CE is counter electrode

TABLE-1
COMPONENTS FOR PRODUCING Ni-P ALLOY BY JET ELECTRODEPOSITION

Composition	Concentration ($g L^{-1}$)	Composition	Concentration ($g L^{-1}$)
$NiSO_4·6H_2O$	400	H_3PO_4	50
$NiCl_2·6H_2O$	100	$C_3H_6O_3$	40
H_3PO_3	50	$CH_3(CH_2)_{11}SO_3Na$	0.08
H_3BO_3	50	H_2NCSNH_2	0.01

Electrochemical test: Electrochemical test was performed by the three-electrode system. The dynamic parameters of jet electrodeposition were determined by polarization curve measurements carried out during the process. Polarization curves were obtained by potential sweep method, with a potential scanning from -1 V to +1 V and a scanning speed of 5 mV s^{-1}. All potential values were given with respect to the reference electrode.

RESULTS AND DISCUSSION

When the polarization current density is large, but not enough to cause concentration polarization, the electrochemical polarization basic equations are[6]:

$$\Delta\varepsilon_k = -\frac{2.3RT}{\alpha nF}\log i_0 + \frac{2.3RT}{\alpha nF}\log i_k \quad (1)$$

$$\Delta\varepsilon_a = -\frac{2.3RT}{\beta nF}\log i_0 + \frac{2.3RT}{\beta nF}\log i_a \quad (2)$$

where, $\Delta\varepsilon_k$ is the cathodic superpotential, $\Delta\varepsilon_a$ is the anodic superpotential, T is the temperature, F is the Faraday constant, R is the ideal gas constant, n is the electron number involved in the reaction, α is the cathodic transfer coefficient, β is the anodic transfer coefficient, i_0 is the exchange current density, i_k is the cathode current density and i_a is the anodic current density. There are three basic dynamic parameters in this expression: i_0, α and β. i_0 denotes the oxidation-reduction reaction speed on the electrode under the situation of balance potential and it describes the reversibility of electrode reaction. When i_0 is large, the reaction equilibrium cannot be destroyed easily and the reversibility of the reaction is high; while i_0 is small, then the equilibrium is destroyed easily and the reversibility of the reaction is low. α and β denote the impact of overpotential on the activation energy of electrode reaction[7].

By using the method of Tafel plots to obtain the values of dynamic parameters, eqns. 1 and 2 turn into the form of classic Tafel equation (η = a + b log i):

$$b_k = \frac{2.3RT}{\alpha nF} \quad (3)$$

$$b_a = \frac{2.3RT}{\beta nF} \quad (4)$$

The slopes of Tafel lines are obtained by fitting the polarization curve and the values of α and β can be obtained by bringing slopes into the eqns. 3 and 4. The values of i_0 and E_0 can be obtained from two Tafel lines intersection, by locating the exchange current density (i_0) on the horizontal axis and the equilibrium potential (E_0) on the vertical axis.

Characterization of Ni-P deposition layer: The Ni-P deposition layer, obtained after 5 min of jet electrodeposition under the process conditions shown in Table-1, was found to be smooth and bright to naked eyes. A rasp test result indicated good adhesion to the 45 carbon steel substrate. Characterized by Hitachi S-4800 SEM (scanning electron microscope), the surface of the Ni-P alloy coating appeared to be dense and smooth (Fig. 2).

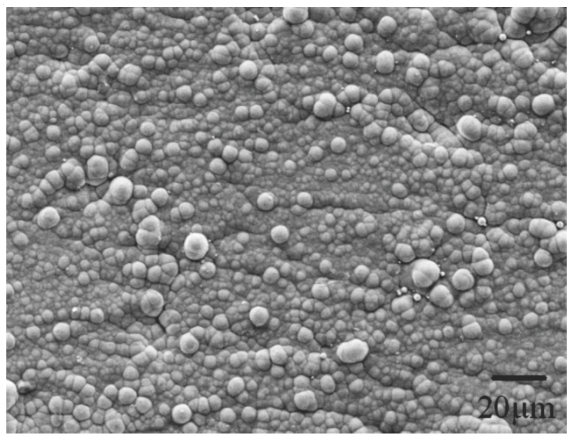

Fig. 2. Surface appearance of Ni-P alloy coating

Influence of temperature on the dynamic parameters: Fig. 3 shows that the polarization curve of Ni-P alloy varied with the temperature (60, 70 and 80 ºC) in the jet electrodeposition process, with constant dipolar space of 1.0 mm and electrolyte flow velocity of 1 ms^{-1}. Fig. 3b is partial enlargement drawing of Fig. 3a.

The influence on dynamic parameters of temperature was compared though Fig. 3. As can be seen, when the temperature was 60 ºC, the equilibrium potential of jet electrodeposition Ni-P alloy system was -0.43962 V and the exchange current density was 0.35886 × 10^{-2} A cm^{-2}. The equilibrium potential of system shifted to lower value with the increased temperature, along with an increase of the exchange current density. When the temperature was 80 ºC, the equilibrium potential was -0.45407 V and the exchange current density was 0.48688 × 10^{-2} A cm^{-2}.

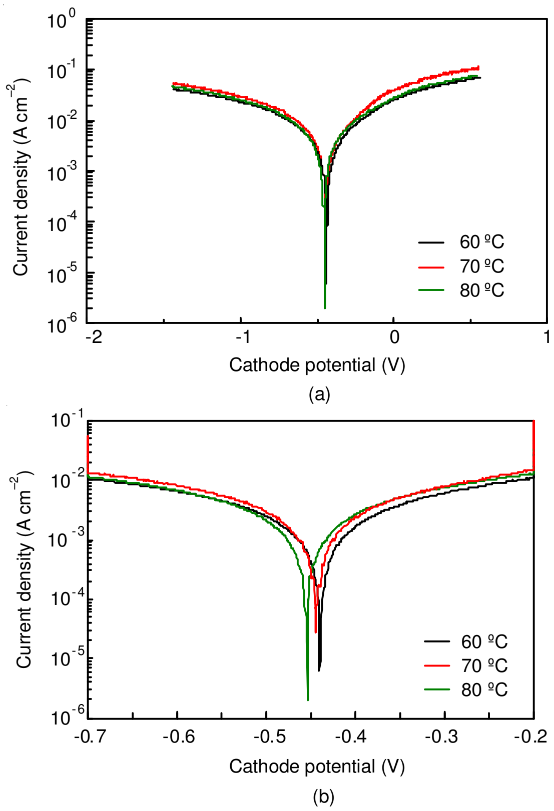

Fig. 3. Cathodic polarization curves at different temperatures

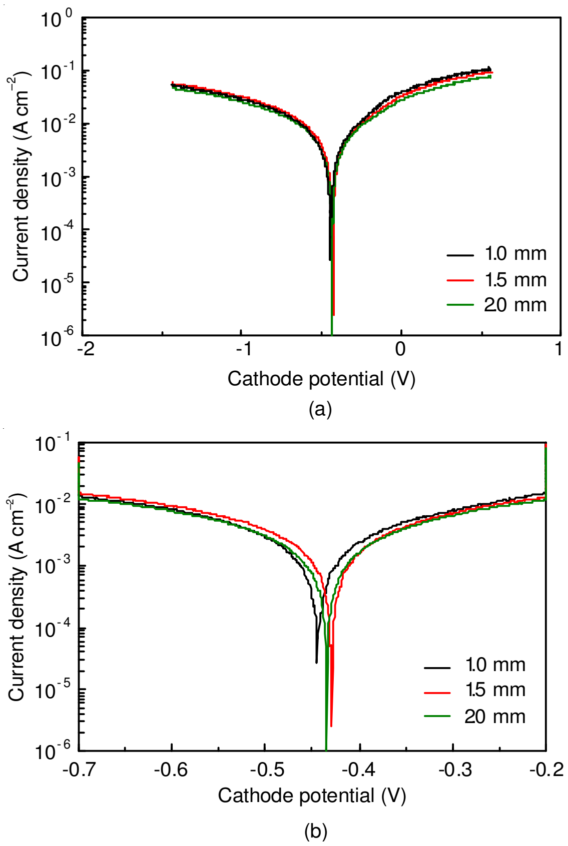

Fig. 4. Cathodic polarization curves with different spaces between the two electrodes

The changes of equilibrium potential and exchange current density were 14.45 mV and 1.28 mA cm^{-2}, respectively. Therefore, the effect of temperature on the equilibrium potential and exchange current density was small and it had subtle impact on the reversibility of system.

Table-2 lists the electrochemical dynamic parameters at different temperatures. As can be seen, the cathodic transfer coefficient α decreased with the increasing temperature, which led to an increase of the reduction reaction velocity, characterized by the negative shift of the polarization curve in Fig. 3.

When the polarization current density is very small, there is a relationship between the polarization resistance Rr and the exchange current density as follows[8]:

$$Rr = \frac{RT}{nF} \cdot \frac{1}{i_0} \quad (5)$$

Apparently, the polarization resistance of jet electrodeposition Ni-P alloy system decreased with the increasing temperature which improved the ion activity and accelerated the ion diffusion and transportation.

Influence of dipolar space on the dynamic parameters: Fig. 4 shows that the polarization curve changed with the dipolar space (1.0 mm, 1.5 mm and 2.0 mm) in the Ni-P alloy jet electrodeposition process, with constant electrolyte temperature of 70 °C and electrolyte flow velocity of 1 ms^{-1}. Fig. 4b is partial enlargement drawing of Fig. 4a.

As can be seen from the figure, when the dipolar space was 1 mm, the equilibrium potential of jet electrodeposition Ni-P alloy system was -0.45228 V and the exchange current density was 0.43827 × 10^{-2} A cm^{-2}. The equilibrium potential of system shifted negatively first and then positively with the increasing dipolar space, along with an increase first and then decrease of the exchange current density. When the dipolar space was 1.5 mm, the equilibrium potential and exchange current density reached the maximum values of -0.45407 V and 0.51827 × 10^{-2} A cm^{-2}, with the changes of 14.32 mV and 1.06 mA cm^{-2}, respectively. It can be seen that the effect of dipolar space on the equilibrium potential and exchange current density was very little and it had small impact on the reversibility of system.

Table-3 lists the electrochemical dynamic parameters with different dipolar spaces. As can be seen, the cathodic transfer coefficient α first increased and then decreased with the increasing dipolar space. Thus, the velocity of reduction reaction first decreased and then increased, which was characterized by the shift of polarization curve in Fig. 4. The value of polarization resistance Rr of the jet electrodeposition Ni-P alloy system was obtained according to the eqn. 5, which first decreased and then increased with the increasing dipolar space.

TABLE-2
ELECTROCHEMICAL DYNAMIC PARAMETERS AT DIFFERENT TEMPERATURES

Temperature (ºC)	Cathode slope	Anode slope	Equilibrium potential (V)	Transfer coefficient (α)	Transfer coefficient (β)
60	0.43385	0.40127	-0.43962	0.480493	0.519507
70	0.40204	0.36756	-0.44312	0.479625	0.520375
80	0.51429	0.46449	-0.45407	0.474560	0.525440

TABLE-3
ELECTROCHEMICAL DYNAMIC PARAMETERS WITH DIFFERENT SPACES BETWEEN THE TWO ELECTRODES

Dipolar space (mm)	Cathode slope	Anode slope	Equilibrium potential (V)	Transfer coefficient (α)	Transfer coefficient (β)
1.0	0.40204	0.36756	-0.44312	0.479625	0.520375
1.5	0.46610	0.44873	-0.42880	0.490506	0.509494
2.0	0.48795	0.45358	-0.43448	0.481748	0.518252

TABLE-4
ELECTROCHEMICAL DYNAMIC PARAMETERS WITH DIFFERENT FLOW VELOCITIES

Flow velocity (m s^{-1})	Cathode slope	Anode slope	Equilibrium potential (V)	Transfer coefficient (α)	Transfer coefficient (β)
0.5	0.45574	0.43892	-0.43078	0.490599	0.509401
1.0	0.40204	0.36756	-0.44312	0.479625	0.520375
1.5	0.34123	0.31528	-0.43241	0.480237	0.519763

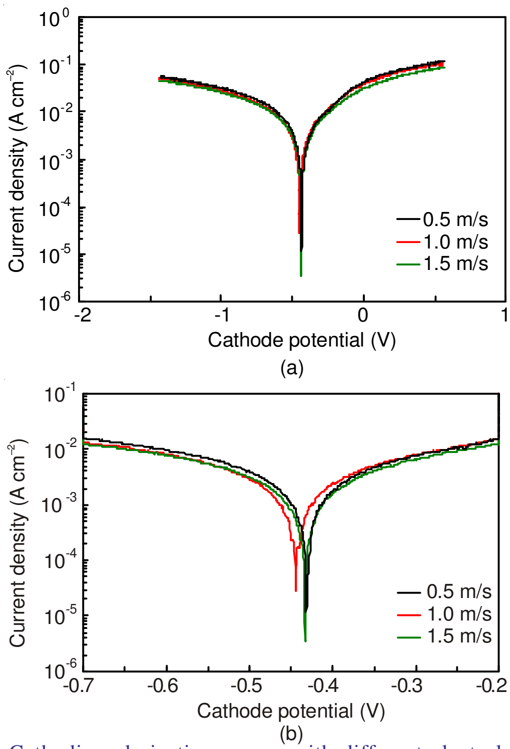

Fig. 5. Cathodic polarization curves with different electrolyte flow velocities

Influence of electrolyte flow velocity on the dynamic parameters: Fig. 5 shows that the polarization curve changed with the electrolyte flow velocity (0.5, 1.0 and 1.5 m s^{-1}) in the Ni-P alloy jet electrodeposition process, with constant electrolyte temperature of 70 ºC and dipolar space of 1.0 mm. Fig. 5b is partial enlargement drawing of Fig. 5a.

As can be seen from the figure, when the electrolyte flow velocity was 0.5 m s^{-1}, the equilibrium potential of jet electrodeposition Ni-P alloy system was -0.43078 V and the exchange current density was 0.53351×10^{-2} A cm^{-2}. The equilibrium potential of the system shifted negatively first and then positively with the increasing flow velocity, along with a decrease of exchange current density. When the electrolyte flow velocity was 1.0 m s^{-1}, the equilibrium potential reached the minimum of -0.44312 V. When the electrolyte flow velocity was 1.5 m s^{-1}, the exchange current density reached the minimum of 0.30615×10^{-2}A cm^{-2}. The changes of equilibrium potential and exchange current density were 12.34 mV and 2.27 mA cm^{-2}, respectively. The electrolyte flow velocity strongly affected the equilibrium potential and exchange current density and it had the highest impact on the reversibility of system, compared with the temperature and dipolar space.

Table-4 lists the electrochemical dynamic parameters with different flow velocities. As can be seen, the cathodic transfer coefficient α decreased first and then increased with the increasing flow velocity. As a result, the velocity of reduction reaction increased first and then decreased, which was characterized by the shift of polarization curve in Fig. 5. Calculated using the eqn. 5, the polarization resistance of jet electrodeposition Ni-P alloy system increased with the increasing electrolyte flow velocity.

Conclusion

The following conclusions can be drawn: Within the range of experiments, the electrolyte temperature had subtle impact on the reversibility of the system and the velocity of reduction reaction increased with the increasing electrolyte temperature. This can be mainly attributed to that the diffusion and migration rate of reactive ions were improved with the increasing electrolyte temperature. The dipolar space had small impact on the reversibility of the system. The velocity of reduction reaction first decreased and then increased with the increasing dipolar space, which may be related to the activation energy of reduction reaction. The electrolyte flow velocity had the greatest impact on the reversibility of the system, compared with the temperature and dipolar space. The velocity of reduction reaction increased first and then decreased with the increasing electrolyte flow velocity, which was mainly caused by the electrolyte pressure and turbulence degree.

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