Rare Metal Materials and Engineering
Volume 44, Issue 2, February 2015
Online English edition of the Chinese language journal

Available online at www.sciencedirect.com
ScienceDirect

Cite this article as: Rare Metal Materials and Engineering, 2015, 44(2): 0312-0318.

ARTICLE

Microstructure and Properties of Nickel Layers Electrodeposited under Reduced Pressure and Temperature Gradient Conditions

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Abstract: Our previous studies showed that at a considerably high plating speed up to 1 mm/h, the nickel electrodeposits with smooth surface, few deposition defects and some improved properties could be prepared under the conditions of an additive-free bath at a reduced pressure of 5 kPa and a temperature gradient of 35 °C /65 °C. This paper aims at further analyzing the effect of bath pressure and temperature gradient on the surface morphology, the microstructure and the properties of electrodeposited nickel coatings in a subatmospheric environment. Our findings indicate that the surface quality, the microstructure and the properties of the deposited nickel coatings are, to some extent, affected by the applied bath pressure and the temperature gradient; favorable nickel electrodeposits can be only achieved when the electrolyte in the vicinity of cathode surface is in a boiling state. The temperature gradient influences the texture characteristic of nickel deposits, but the bath pressure has few effects on the preferred orientation. Grain-fining, microhardness, and corrosion resistance of nickel deposits are improved with increasing of the temperature-gradient and/or the reducing of bath pressure. These variations are closely relevant with the boiling-driven mass transfer effect and the vacuum-degassing effect during the electrodeposition in a reduced pressure bath

Key words: electrodeposition; reduced pressure; microstructure; acid resistance; temperature gradient

To further improve the surface morphology and the performances of the plated coatings, some pressure assisted plating processes have been employed. Tsai et al.[1] prepared nickel deposit featuring few pinhole defects and fine grains at a high pressure of 318.8 kPa, and found that the microhardness of the electrodeposit was increased by about 20% than those deposited from a normal environment. On the contrary, Pessel[2] electroplated chromium coatings in a reduced pressure bath and obtained some favorable results. After that, the reduced pressure electroplating technique has attracted more attentions and was further developed[3-7]. The studies by Anon[3] indicated that chromium coatings from a reduced pressure bath have little porosity, few crack networks, fine grains and good adhesion with substrate. Dini *et al*.[4] reported their investigations on electroless plating nickel (bath pressure, 66.5 kPa) and electroplating copper(bath pressure 13.3 kPa) processes, and concluded that a subatmospheric environment helped to reduce pinholes and surface roughness, and improved compactness of coatings with finer grains. Nam *et al*.[5] implemented the electrodeposition process in a vacuum environment (53~80 kPa), preparing a kind of pinhole-free and ultrastable Pd-Ni alloy composite membrane for catalysis applications. Recently, we have electroformed some nickel microparts with few voids and good surface quality under the periodic vacuum-degassing and constant temperature-gradient conditions[6,7]. Degassing, eliminating of gas bubble, reducing of the introduction of oxidation and particle contamination from an atmospheric environment are generally considered as the main contributions to achieve those favorable coatings in a subatmospheric plating bath.

Lately, our findings[8] further showed that without additives, favorable nickel electrodeposits with smooth surface,

Received date: March 25, 2014
Foundation item: National Natural Science Foundation of China(51175152) and Program for Science and Technology Innovation Talents in Universities of Henan Province (2012HASTIT012)
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few voids and some improved properties can be prepared at a significantly high plating rate of 1 mm/h if a constant bath pressure of 5 kPa and a constant temperature gradient of 35°C/65 °C between bulk electrolyte and cathode are applied to the electroplating bath. However, little information about the effect of bath pressure and temperature-gradient on the surface morphology and the properties of electrodeposited nickel has been presented so far. This paper aims at further analyzing the surface morphology, the microstructure and the properties of nickel plated at different reduced bath pressures and temperature-gradients.

1 Experimental

The apparatus and some operating conditions used in this study were described in detail in Ref.[8]. Two heating pipes were installed in the cathode unit and the cell. to heat the cathode surface and the bulk electrolyte. To form different temperature gradient between the bulk electrolyte and the cathode surface on the premise of avoiding decomposition of the bath components, the bulk electrolyte was kept at (35±1) °C, and then changed from 40 °C to 65 °C. The bath pressure was controlled in the range of 20~5 kPa by a vacuum-adjusting valve to prevent the bulk electrolyte from boiling at any temperature gradient set above. No extra stirring was applied to the bulk electrolyte. To reduce loss of the bath solution, the evaporated components were continually recycled to the bath by a condensation-recycling apparatus developed by ourselves[9]. The coating thickness was about 80 μm by controlling the electrodeposition time. The applied current density was kept at 0.09 A/cm^2.

The cathode polarization curves were recorded by an electrochemical workstation (PAR 2273, USA) with a sweep rate of 20 mV/s. The surface morphology of deposits was examined by a digital camera (Canon 5D Mark II, Japan) and a scanning electron microscope (JSM-6300, Japan). A transmission electron microscope (Tecnai G2 F30 S-TWIN, USA) and an X-ray diffractometer (D/max 2500VL/PC, Japan) were used to characterize the microstructure. The calculation of the preferred orientation degree of nickel deposits was described in Ref.[10].

Microhardness tests were performed using an intelligent digital microhardness tester (HXS-1000A, China) with a load of 980 mN exerted for 10 s. The microhardness of deposited sample is the average of seven measurements in different places.

Corrosion resistance is reflected by the corrosion rate, which is the ratio of corrosion mass loss to total mass of the deposit before corrosion. The corrosion rate was measured using a mass-loss method, and the corrosion process was carried out in a 10 wt% HCl solution and a 10 wt% H_2SO_4 solution for a total of 14 d. Before and after corrosion, the deposits were washed with distilled water and acetone for several times, dried in vacuum, and then subjected to related test and analysis. A precision electronic balance (Mettler Toledo, Switzerland) with a precision of 0.1 mg was used to weigh the mass before and after corrosion.

2 Results and Discussion

2.1 Cathodic polarization curves

Fig.1 shows the cathodic polarization curves obtained at different bath pressures and the same temperature gradient of 35 °C/65 °C. The cathodic polarization curves obtained at all applied bath pressures of 5, 10, 15, 20 and 25 kPa, have almost the same change trend, indicating that cathode electrode process experiences successively four regions: linear, activation, mixed mode of activation and mass transfer, and limiting current density, with increasing of the applied potential. However, the limiting current density, defined as the maximum current density that can be used to obtain a desired electrode reaction without undue interference such as from polarization, obtained at various bath pressures is significantly different. The limiting current densities measured from the relatively high pressure, i.e., 15, 20 and 25 kPa, are almost the same, 0.07 A/cm^2, while the ones obtained at the pressures of 10 and 5 kPa increase surprisingly to 0.4 and 0.9 A/cm^2, respectively. These changes indicate that reducing of bath pressure contributes to the increase of the limiting current density of cathode electrode process. Since the limiting current density is mainly dependent on a diffusion layer thickness which is inversely proportional to mass transfer rate, a vigorous convection-driven mass transfer may rationally exist in the vicinity of electrode surfaces in those baths with lower pressure. This kind of vigorous convection rationally comes from the boiling-related effect convection as no other external stirring is applied to the electrolyte. These results also agree well with our experimental observations. At 5 kPa, the vigorous boiling phenomena can be observed regardless of the applied current density, which is because the electrolyte very close to the cathode surface is heated to reach or surpass boiling point when a temperature gradient of 35 °C/65 °C is imposed. Such boiling phenomena feature

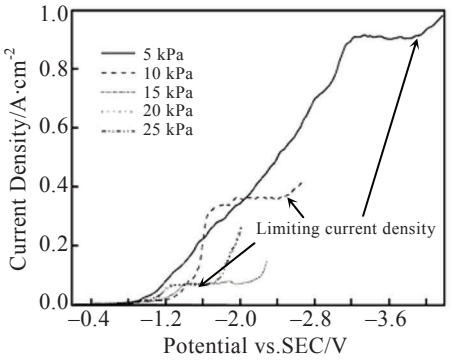

Fig.1 Cathodic polarization curves measured at different subatmospheric pressures and a temperature gradient of 35 °C /65 °C