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Electrodepositing Nickel under Electrolyte Reduced-pressure Boiling Condition

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ABSTRACT

A non-traditional electrodeposition technique carried out under the condition of electrolyte reduced-pressure surface-boiling is presented in this paper. Using this kind of technique, favorably smooth nickel coatings without pinholes and nodules are unexpectedly plated at a rate of up to 0.81 mm/h from an additive-free bath. Analysis using SEM, TEM and XRD indicates that, microstructure and properties of the nickel coatings change with increasing of applied current density. The nickel prepared electrochemically from a reduced-pressure boiling bath at 40A/dm^2-69A/dm^2 have a considerably high microhardness with a range of 300HV-500HV and a good acid resistance. In addition, it features a preferred orientation crystal face of (220). The change in the electrodeposition rate, microstructure and properties of the reduced-pressure electrodeposited nickel coatings mainly results from the comprehensive effects of vacuum degassing and boiling dynamics. The latter involves nucleation, growth, coagulation and burst of boiling bubble and can provide the nickel deposition process with several positive actions

1. Introduction

Electrodeposition is a widely used process to make metal coatings and articles and has three typical forms of application, i.e., electroplating, brush electroplating and electroforming [1]. Further improving surface quality and properties of electrodeposited coatings and articles has always been the most important object in this area. For this object, besides optimizing operating conditions and electrolyte compositions, researchers have developed some special plating techniques, such as pressure aid electrodeposition [2], super gravity assisting electrodeposition [3] and reduced pressure electrodeposition processes [4–13], etc. Among them, the reduced pressure electrodeposition processes have received more attentions due to their some unique advantages. The reduced pressure electroplating process may date back to 1945 when subatmospheric pressure was first introduced into the apparatus for the electroplating of iron, manganese, etc., to reduce oxidation and pinhole defects by Leopold [4]. After that, Becker [5] further improved the reduced pressure plating apparatus. Then, the investigations [6,7] on deposition mechanism, property evaluation and application development of chromium electroplating in a subatmospheric pressure bath have been thoroughly made and showed the chromium coatings featuring smooth surface, few pits and microcracks, and fine grains can be plated from a subatmospheric pressure bath (>40 kPa) with a considerably high efficiency. They also indicated that the coatings had an appreciatively strong adhesion to cast iron substrates and thus were well used to various articles, such as piston rod, piston ring, cylinder liner and mould, etc. In 1991, Zhu [8] proposed a pressure-alternating (ambient pressure and subatmospheric pressure) method to eliminate gas bubbles and implement air agitation intermittently during electrodeposition. In 1992, after researching on electroless plating nickel (66.5 kPa) and electroplating copper (13.3 kPa), Dini et al. [9] reported conclusively that the reduced pressure helped to decrease pinholes and surface roughness, refine grains and improve compactness of the coatings significantly. Nam et al. [10,11] prepared electrochemically pinhole-free palladium alloy coatings with superstable and excellent catalytic properties using the reduced pressure process. By forming a temperature-gradient between cathode surface (high temperature) and bulk electrolyte (low temperature) to promote a temperature-gradient-driven natural convection effect, we improved a pressure-alternating electrodepostion technique and fabricated some favorable nickel microparts [12,13].

Under some circumstances, mass transfer is vital to the electrodeposition process. For instance, poor convection within microrecesses is usually the main reason for the failure of high aspect-ratio microelectroforming. On the other hand, mass transfer manner and flow velocity in the vicinity of cathode surface may, to some extent, determine plating rate, microstructure and properties of electrodeposited coatings. Therefore, electroplating processes with a special mass transfer manner, such as electrolyte

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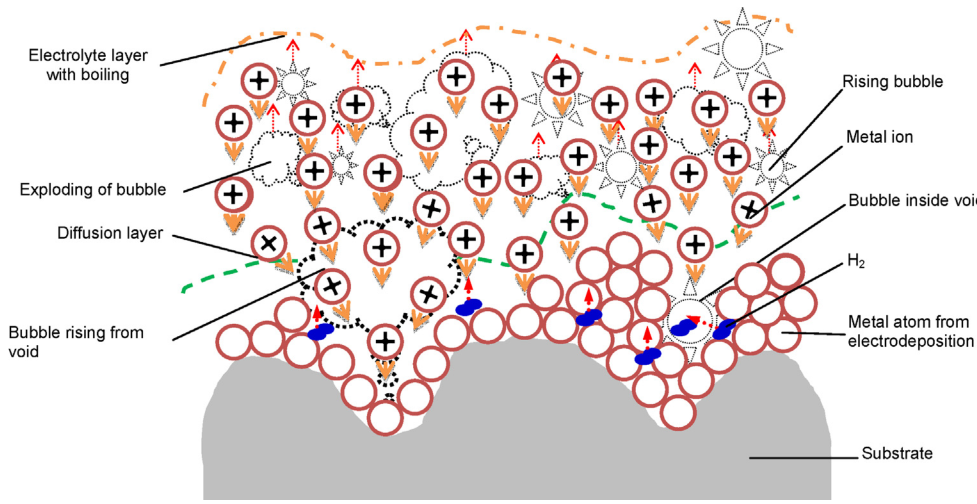

Fig. 1. Schematic diagram of electrolyte reduced-pressure surface-boiling electrodepositon.

jet electrodeposition [14], ultrasonic/megasonic stirring electrodeposition [15,16], magnetic convection electrodeposition [17], hard particle abrasion electrodeposition [18], generally offer a distinctive microstructure and/or plating rate. As a rule, excellent mass transfer conditions can potentially lead to a satisfactory electrodeposition rate.

However, the reduced pressure electrodeposition processes mentioned above haven't exhibited a high-speed characteristic. In fact, the electrolyte in a subatmospheric pressure electroplating bath can be easily boiled at low temperature and the boiling then can cause a vigorous convection mass transfer as well as some special hydrodynamic and thermal effects. These boiling-related actions might further promote the reduced pressure electrodeposition process, but have not been applied to the cathodic deposition before. Therefore, we proposed a modified reduced pressure electrodeposition process in which only the electrolyte in the vicinity of cathode surface is kept boiling [19]. By using our proposed reduced pressure technique, significantly smooth nickel coatings were produced at a rate of about 0.762 mm/h in the presence of some additives. This paper will focus on investigating nickel electrodeposition in an electrolyte reduced-pressure boiling state in the absence of any additives which hasn't been reported before.

2. Theoretical analysis

The working mechanism of the electrolyte reduced-pressure boiling electrodeposition is illustrated in Fig. 1. During boiling, numerous bubbles are first preferentially impregnating within some microrecesses of depositing surface (cathode surface), and then evolve accompanying with a series of actions: growing, moving, coalescing, rising, swelling, collapsing or bursting [20]. Due to these actions, a variety of special agitations, such as streaming, jetting, pumping, etc., could be triggered in the vicinity of cathode surface [20,21], probably resulting in an extremely thin diffusion layer [22]. Under such conditions, a remarkably high deposition rate may be achieved. What's more, the above-mentioned microrecesses where mass transfer is generally poor may be filled with stirred electrolyte also owing to the boiling bubble actions, and thus the leveling of electrodeposited coatings may be improved. In addition, grain growth which is most likely to originate from the foregoing microrecesses may be affected by the bubble actions. Therefore, with these unusual effects, some aspects of the reduced-pressure boiling electrodeposition process, for example, deposition rate and microstructure of electrodeposited coating, can be different from those from the other electrodeposition processes including the previous reduced pressure electrodeposition processes.

3. Experimental

The experiments were carried out in a special setup, shown in Fig. 2. It mainly consists of sealed transparent cell (maximum volume is two liters), power supply, anode assembly, cathode assembly, cathode temperature control unit, bulk electrolyte temperature control unit, vacuum pump, vacuum regulating valve, vacuum gauge, recycling system of evaporated substance, and circulation & filtration unit(not shown in Fig. 1). The vacuum regulating valve located on the cover of cell is used to regulate bath pressure in real-time. The cathode is installed horizontally in the cell to facilitate gas and bubble to escape. Two temperature control units are set to control the temperature of bulk electrolyte and the electrolyte very close to the cathode surface, respectively. During electrodeposition, to reduce evaporation loss, only the electrolyte in the vicinity of cathode surface was kept boiling. The additional recycling system of evaporated substance is, to large extent, to keep the solution compositions unchanged. The inlet and outlet of the circulation & filtration unit were both far away from the cathode surface to reduce hydrodynamic effect on the boiling actions. During electrodeposition, the circulation &

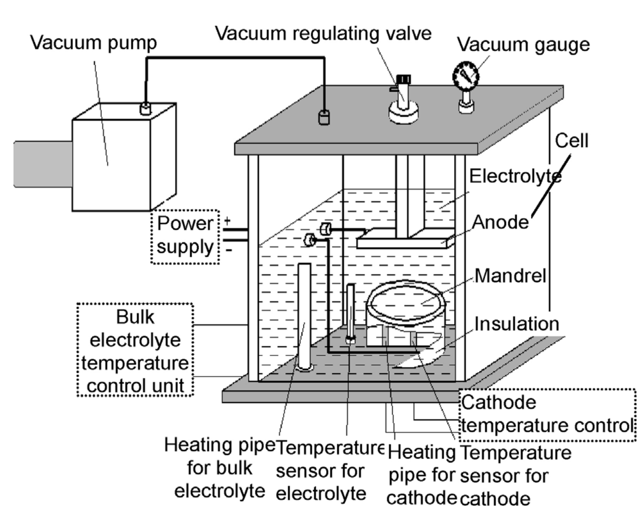

Fig. 2. Experimental setup of electrolyte reduced-pressure surface-boiling electrodeposition.