Surface & Coatings Technology 270 (2015) 123–131

Contents lists available at ScienceDirect

Surface & Coatings Technology

journal homepage: www.elsevier.com/locate/surfcoat

Electrodeposition of nanocrystalline nickel assisted by flexible friction from an additive-free Watts bath

Biao Lv [a,b,*], Zhenfeng Hu [c], Xiaohe Wang [b], Binshi Xu [b]

[a] School of Materials and Metallurgy, Northeastern University, Shenyang 110819, China
[b] National Key Laboratory for Remanufacturing, Academy of Armored Forces Engineering, Beijing 100072, China
[c] National Engineering Research Center for Mechanical Products Remanufacturing, Academy of Armored Forces Engineering, Beijing 100072, China

ARTICLE INFO

Article history:
Received 14 November 2014
Accepted in revised form 4 March 2015
Available online 12 March 2015

Keywords:
Electrodeposition
Nanocrystalline nickel
Flexible friction
Preferred orientation
Microhardness

ABSTRACT

Nanocrystalline nickel coatings with different grain sizes were prepared by a modified electrodeposition technology assisted by flexible friction from an additive-free Watts bath. The effects of various flexible media, e.g. polymers, bio-bristles and natural fibers, on the morphology, preferred orientation, and grain size of electrodeposited nickel coatings were studied at different temperatures. The results demonstrate that flexible friction can effectively hinder the aggregation growth of adsorbed atoms and remove some surface-adsorbed species, to significantly refine the grain size and change the preferred orientation of deposits. The crystal growth inhibition effect significantly increases with temperature and incremental contact pressure of flexible friction. At 50 °C, the nanocrystalline nickel coating gained by bio-bristle friction is the smoothest and has a dense surface morphology with a (111) preferred orientation. The corresponding grain sizes concentrate in the range of 20–30 nm, and the microhardness is between 470 and 500 HV, which is higher than that of the traditional electrodeposited nickel coating (320 HV). The grain refining mechanism, texture evolution and microhardness variation of nickel deposits assisted by flexible friction are discussed.

1. Introduction

A nanocrystalline nickel coating has been widely studied in fundamental research and in engineering applications due to its excellent properties, such as high hardness [1], strength [2–4], wear resistance [5], anti-fatigue [6] and localized corrosion resistance [7,8]. Electrodeposition has been widely recognized as a feasible and economic technique for producing dense nanocrystalline nickel coatings [9]. In a traditional nickel electroplating process, organic additives, e.g. saccharin, and 2-butyne-1,4-diol, are necessary to lower the grain growth rate [9–14]. However, these organic additives usually result in inclusions of surface-active elements such as sulfur and carbon in the deposits, which segregate out to the grain boundaries and adversely affect some of the properties (mechanical, magnetic and/or anti-corrosion) [12,15–19].

To eliminate the disadvantages of the bath additives, mechanical attrition or physical friction was introduced to the electrodeposition process. Xu et al. [20,21] reported that using a graphite anode wrapped in a piece of cotton to rub against the surface, enabled the preparation of nickel and nickel-based nanocomposite coatings which had a higher degree of hardness than those of nickel coatings electroplated in the traditional bath. NET methods [22] were invented to friction the cathode surface by means of adding hard particles of SiC, SiO_2, and Al_2O_3 to the bath, which improved the deposition rate and the quality of deposits. Liang and Xie[23] developed a friction and spray electroplating technique which combined the merits of diamond block rubbing and jetting, and achieved a fast electrodeposition of bulk nickel coatings. Ning and He[24] put forward a mechanical attrition (MA) method by the vertical movement of glass balls with a special vibrating frequency on the sample surface, which changed the grain growth direction and microstructure of nickel coatings. Zhu et al. [25] reported that nanocrystalline nickel grain sizes of 30–80 nm can be prepared by an electrodeposition method in combination with the simultaneous polishing of free particles. This method modified the mechanical properties of rotating parts. In summary, mechanical polishing or physical friction can improve the structure and facilitate the synthesis of nanocrystalline nickel coatings. However, the friction material is either used as a soft sheath, or as non-conductive hard particles and a friction block. The former is difficult to apply to the automatic electroplating industry due to its poor wear resistance, while the latter is inconvenient in the assembling, replacement and cleaning stages.

In this paper, three types of flexible media, namely, polymers, bio-bristles and natural fibers, were adopted for electrodepositing nanocrystalline nickel coatings from an additive-free Watts bath.

* Corresponding author at: School of Materials and Metallurgy, Northeastern University, Shenyang 110819, China. Tel.: +86 010 66717351.
E-mail address: lb594287163@126.com (B. Lv).

http://dx.doi.org/10.1016/j.surfcoat.2015.03.012
0257-8972/

The grain refining mechanism, texture evolution and microhardness variation of electrodeposited nickel coatings are discussed.

2. Experimental procedures

2.1. Electrodeposition of nickel coatings

A schematic illustration of the electroplating apparatus, employing flexible friction, is shown in Fig. 1a. The experimental apparatus was modified based on the conventional cathode moving electroplating device. As seen in Fig. 1b, two brush plates of the same size were introduced and fixed onto the side of the electroplating tank. The brush plate, of dimensions 112 mm × 26 mm × 10 mm, and close-packed flexible media were planted in the plate. The diameter of a single bundle of flexible medium is 3 mm and the width of each fiber of the flexible medium is approximately 0.2 mm with an exposed length of 15 mm. Furthermore, three classes of non-conductive flexible media with different physico-chemical properties, i.e. polymers (PA, PP), bio-bristles (horsetails, bristles) and natural fibers (palm fiber), were selected as flexible friction media, and the contact length was kept at about 2 mm between the friction media and substrate. Flexible friction is expected to inhibit grain growth during electroplating, which may produce nanocrystalline nickel coatings from an additive-free Watts bath.

Low carbon steel sheets with dimensions of 50 mm × 100 mm × 2 mm and an exposed area of 0.3 dm^2 were used as cathodes. Three-chained electrolytic nickel plates, of 99.97% purity and an exposed surface area 1.2–1.8 dm^2, were used as soluble anodes; the area was greater than the cathodes to avoid strong anodic polarization. The parallel separation of them was approximately 15 mm during electroplating of nickel with flexible friction. Prior to nickel electrodepositing, all substrates successively underwent electrochemical degreasing (cleaning solution), strong activation (activating solution #2) and weak activation (activating solution #3) and complete rinsing with distilled water between every two steps. The specific pretreatment process was described in reference [26]. After the pretreatment, nickel coatings were electrodeposited onto the substrate without/with flexible friction. The detailed bath composition and operating parameters fornickel electrodepositing assisted by flexible friction are presented in Table 1.

2.2. Characterization of nickel coatings

Surface and cross-sectional morphologies of the electrodeposited nickel coatings were observed by a Philips Quanta200 scanning electron microscope (SEM). The surface roughness of nickel coatings was estimated by a LEXT OLS4000 3D measuring laser microscope, and the average value was given after three testings. The microstructure of nickel coatings was analyzed by a JEM-2100 transmission electron microscope (TEM), and the grain size distribution was determined using a nano-measurement software for TEM images. The preferred orientation of the deposits was measured by D8 advance multi-crystal X-ray diffraction (XRD), using a Cu target (incident wavelength, $\lambda = 0.15406$ nm), 40 kV, and 40 mA. The preferred orientation of the deposits was characterized by the following texture coefficient $TC_{(hkl)}$[14].

$$TC_{hkl} = \frac{I_{(hkl)}/I_{0(hkl)}}{\sum_{i=1}^{n} I_{(hkl)}/I_{0(hkl)}} \times 100\%$$

where $I_{(hkl)}$ and $I_{0(hkl)}$ represent the X-ray diffraction intensities of (hkl) planes of nickel coatings and the standard nickel powder, respectively; n is the number of diffraction peaks. The value of n is 4 for (111), (200), (220) and (311) crystal planes in the paper. When TC values of each plane are the same, it indicates a preferred-free orientation. If $TC_{(hkl)}$ of some crystal face is 25% greater than the average value, it is considered as a preferred orientation. The larger the $TC_{(hkl)}$ value, the

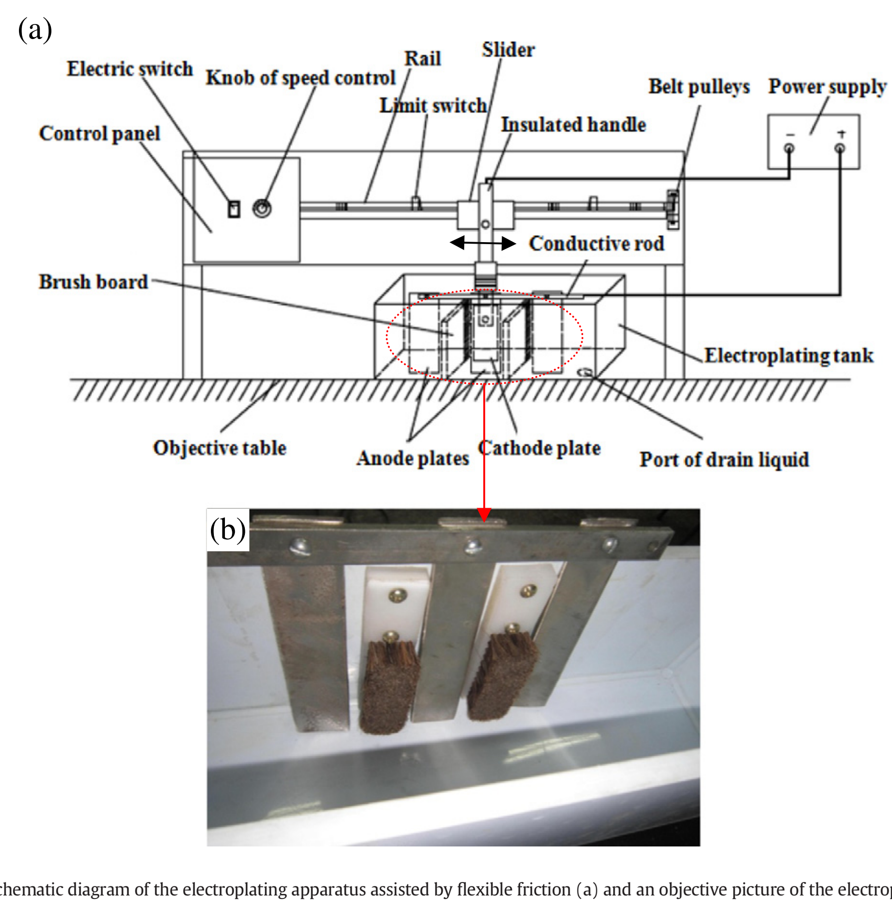

Fig. 1. A schematic diagram of the electroplating apparatus assisted by flexible friction (a) and an objective picture of the electroplating tank.