Journal of Alloys and Compounds 557 (2013) 228–238

Contents lists available at SciVerse ScienceDirect

Journal of Alloys and Compounds

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

Establishing relationships between electrodeposition techniques, microstructure and properties of nanocrystalline Co–W alloy coatings

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ARTICLE INFO

Article history:
Received 26 October 2012
Received in revised form 1 January 2013
Accepted 2 January 2013
Available online 11 January 2013

Keywords:
A. Coating materials
A. Metals and alloys
B. Precipitation
C. Microstructure
C. Mechanical properties
C. Corrosion

ABSTRACT

Nanocrystalline cobalt–tungsten (Co–W) alloy coatings with varying microstructures were produced by different electrodeposition techniques. The properties, including hardness, friction and wear behavior, and the resistance to electrochemical corrosion, of the nanocrystalline Co–W alloy coatings are strongly dependent on their microstructures and compositions that are determined by the electrodeposition techniques used. The hardness of the coatings increases with decreasing average crystallite size and increasing W content in alloy. The increasing W content and decreasing surface roughness favor the improvement of the resistance to corrosion for Co–W alloy coatings. The tribological properties and the corresponding wear mechanisms of the coatings are closely related to their hardness and microstructures. The wear rates of the coatings are in accordance with Archard's law at high applied load of 10.0 N, that is, their wear rates are linearly proportional to the inverse hardness. However, the surface roughness and morphology of the coatings greatly affect this accordance at the low load of 5.0 N. In general, various pulse electrodepositions is better than the direct current (DC) plating to produce Co–W alloy coatings with smaller crystallite size, higher hardness and the improved wear resistance. The nanocrystalline Co–W alloy coating produced by the bipolar pulse electrodeposition has the highest hardness and the best resistance to wear and corrosion. Finally, the electrodeposition mechanisms involved in these electrodeposition techniques are explained and account for the differences in the microstructure and the properties for these deposits.

1. Introduction

Cobalt and its alloys are widely used as typical magnetic materials applicable in various fields such as micro-electromechanical system (MEMS) devices, magnetic recording head, reading heads and data storage media [1–5]. Wear exists when MEMs devices are in service in many cases. The continuous removal of surface materials decreases the lifetime of the MEMS devices and results in enormous energy and economic loss. Surface coatings are often used as protective layers to decrease the wear and tear so as to increase the lifetime of devices. Electrodeposition is an election technique in preparing alloy coatings for its forming capability, tailoring microstructure and satisfying properties.

Tungsten (W) alloys with iron group metals are of interest now in both theoretical and applied aspects for their specific mechanical, tribological, anti-corrosion, magnetic, electrical and electroerosion properties [6–24]; and may compete even with ceramics and graphite by virtue of high thermal resistance. Binary, ternary, and quaternary tungsten alloys with iron group metals can be obtained from complex solutions such as pyrophosphate, gluconate or citrate based, e.g. nickel–tungsten (Ni–W) [6–15] and cobalt–tungsten (Co–W) [18,22–24] with a nanocrystalline microstructure are considered as hard coatings and possess favorable wear and corrosion properties which make them extremely attractive for replacing hard Cr coatings in many applications. Sriraman et al. [6] produced nanocrystalline Ni–W alloy coatings by DC plating and evaluated the hardness and the sliding wear resistance of the coatings with the variation of their grain size. Argañaraz et al. [15] prepared the nanostructured Ni–W coatings with varying grain size from 65 to 140 nm by pulse electrodeposition and found that the hardness of the coatings varied from 650 to 850 Hv with decreasing grain size. When compared to Ni–W alloy coating, nanocrystalline Co–W is more attractive to replace the hard chromium deposit because the hexagonal close-packed (hcp) structure of Co is better resistance to wear than the face-centered cubic (fcc) structure of Ni [25]. Weston et al. [21] found that the wear resistance of Co–W alloy coating was better than that of electrodeposited chromium under certain sliding conditions.

The structures and properties of the W-containing alloys depend on the electrodeposition conditions and the chemical compositions of the plating bath. Wei et al. [26] confirmed that the organic additive of ethyl methacrylate greatly improved the homogenous of the deposited Co–W thin film. Dulal et al.

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http://dx.doi.org/10.1016/j.jallcom.2013.01.003

Table 1
Compositions in electroplating bath for electrodepositing nanocrystalline Co–W alloy coatings.

Composition	Concentration ($g\,l^{-1}$)
$CoSO_4{\cdot}7H_2O$	112
$Na_2WO_4{\cdot}2H_2O$	50.0
H_3BO_3	19.0
Na_2SO4	100
Sodium citrate	59.0
Sodium dodecylbenzenesulfonate	0.10
Saccharin sodium	2.0

[17,27,28] found that the pH value, the temperature of the electrolyte and the applied potential determined the structures and properties of the electrodeposited Co–W–P alloy coatings. Our previous work suggested that the current density and electrolyte composition greatly affected the microstructure and tribological property of the deposited Co–W alloy coatings [24]. However, besides the electrolyte composition and the deposition current density, the electrodeposition techniques also have a significant influence on the microstructures and properties of the deposited alloy coatings [18,29–32]. Pulse electrodeposition can operate at different modes, including unipolar, reverse and bipolar pulses. The modes and operating parameters of these pulse electrodepositions have important influences on the microstructures and properties, in particular, the tribological and electrochemical corrosion properties of the final coatings. Tao and Li [29] demonstrated that the nanocrystalline copper film produced by unipolar pulse plating exhibited higher hardness, lower friction coefficient and wear rate than the microcrystalline copper film prepared by DC plating. Pellicer et al. [30] found that the reverse pulse electrodeposited Co–Mo alloy coatings had a more compact structure and was less fragile than the DC plated ones. Vazquez-Arenas et al. [31] reported that the unipolar waveform consisting of $-400\,A\,cm^{-2}$, 80% duty cycle and 500 Hz frequency yielded the smoothest and brightest Co–Ni coating with greatly improved properties over that achieved by direct current plating.

Although there are wide interest in pulse electrodeposition, there has been no systematic study on the microstructures and properties of nanocrystalline coatings of tungsten (W) alloys produced by different electrodeposition techniques up to now. In the present work, four electrodeposition techniques, including DC, unipolar pulse, reverse pulse and bipolar pulse electrodeposition, were used to produce nanocrystalline Co–W alloy coatings. The microstructures, compositions and properties of the final Co–W alloy coatings were characterized. Finally, relationships between electrodeposition techniques, the microstructures, and the properties of the resulting nanocrystalline Co–W alloy coatings were established in this work.

2. Experimental

2.1. Electrodeposition of nanocrystalline Co–W alloy coatings

The bath compositions for the electrodepositing nanocrystalline Co–W alloy coatings are given in Table 1. The electrodeposition was conducted using an Intelligent Multiwave Electroplating Equipment supplied by Handan Dashun Electroplating Equipment Co., Ltd., in China. The equipment is capable of generating time-serial forward and reverse currents at variable levels. The average current density for pulse electrodeposition was calculated using formulas recommended by the equipment manufacturer. A copper plate with the dimensions of Ø25.0 × 2.0 mm was used as the working cathodes. Prior to plating, the surface of the copper plate was mechanically polished to a 0.05–0.10 μm surface finish with 400, 600, and 800 grit waterproof sandpapers and cleaned ultrasonically with distilled water and acetone to remove contamination on the substrate surface. A Ø50.0 mm platinum mesh was used as an anode.

DC, unipolar pulse, reverse pulse, and bipolar pulse electrodeposition techniques were used to produce nanocrystalline Co–W alloy coatings in this work. The wave profiles and their corresponding operating parameters for these electrodeposition techniques are shown in Fig. 1 and Table 2, respectively. The nanocrys-

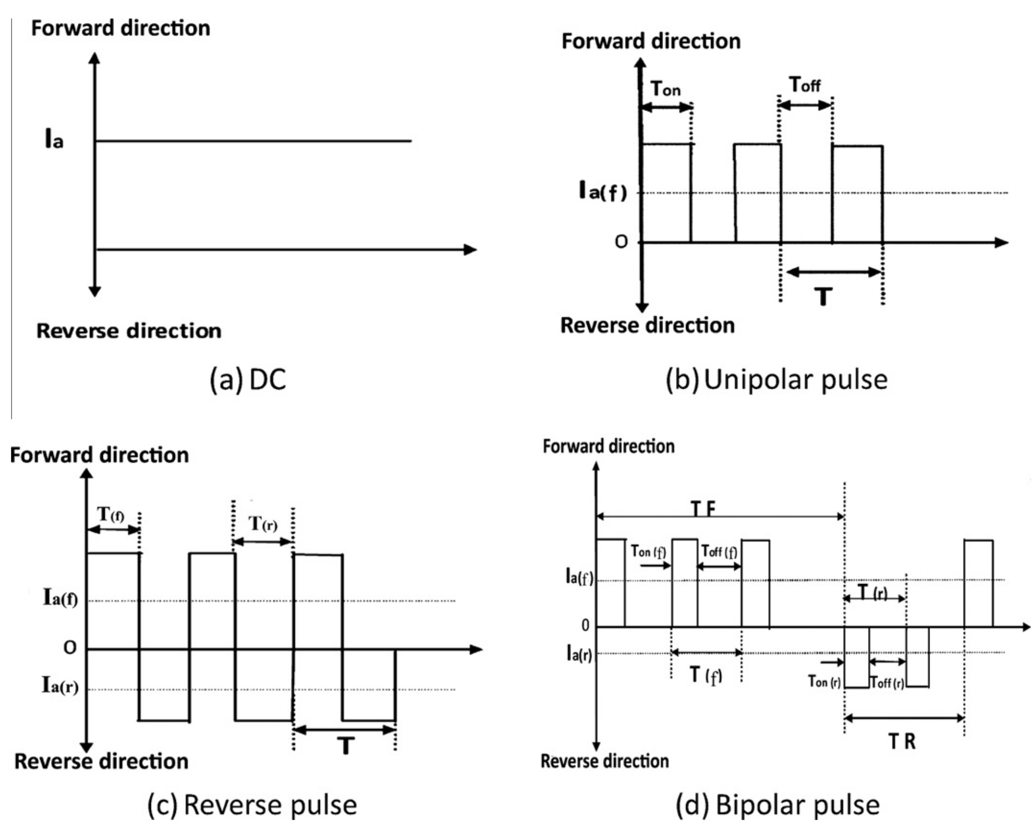

Fig. 1. Electrodeposition wave profiles used for producing nanocrystalline Co–W alloy coatings.