

Fabrication of a nanocrystalline Ni–Co/CoO functionally graded layer with excellent electrochemical corrosion and tribological performance

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Abstract

Nanocrystalline (NC) Ni–Co/CoO functionally graded materials with excellent lubricating, high anti-corrosion and anti-wear performance were fabricated by electrodeposition and subsequent cyclic thermal oxidation and quenching. Transmission electron microscopy and energy dispersive x-ray spectroscopy investigations show that bulk Ni–Co gradient deposits with an average grain size in the range of 13–40 nm demonstrated a graded structure transition from face-centred cubic to hexagonal close packed and graded composition changes from Ni-rich to Co-rich regions with the increase in deposit thickness. X-ray diffraction and x-ray photoelectron spectroscopy analysis indicated the surface layer of NC Ni–Co graded materials to be mainly composed of dense and ultrafine CoO with a (111) preferred orientation. The NC Ni–Co/CoO functionally graded materials exhibited significantly enhanced corrosion resistance in both NaOH and NaCl solutions and remarkably improved wear resistance and dry self-lubricating performance when compared with the NC Ni and Ni–Co graded deposits under dry sliding wear conditions. The higher corrosion and tribological performance of NC Ni–Co/CoO graded materials can be attributed to the graded microstructure within the deposits, the anti-corrosion barrier of a dense oxide layer and the solid lubrication effect of CoO-rich tribo-surface films.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Failures of engineering materials such as friction, wear, corrosion and fatigue often take place on the material surface; surface properties are directly responsible for the performance of the materials. In many engineering applications, surface coatings or deposits are used to increase the lifetime

of components exposed to corrosion or wear conditions. Nanocrystalline (NC) alloy coatings or deposits with a comprehensive combination of excellent adhesion ability with the substrate, high mechanical properties, increased wear resistance and anti-corrosion properties are needed for the design and operation of devices, machines and structural systems in extreme environments [1, 2]. In tribological applications, mechanical properties such as high hardness and

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a lower coefficient of friction are of great importance for the lifetime of tools and components [3]. Grain size reduction for nanocrystalline metals or alloys leads to a significant improvement in hardness and wear resistance [4, 5]. However, the coefficient of friction of NC materials during the wear process is not greatly affected by nanoprocessing—a slightly higher coefficient of friction has even been observed for nanocrystalline metals [6, 7]. In addition, the rate of corrosion of NC materials is usually found to be degraded owing to the metastable microstructure and high volume fraction of the grain boundaries (GBs) [8]; this greatly limits their practical utility. Thus, nanocrystalline deposits or coatings with a unique combination of high strength, better corrosion resistance and superior friction and wear properties would be ‘ideal’ advanced materials for a wide range of functional applications.

The key to fabricating such an ideal surface layer is to design and control the composition and microstructure within the deposits, with the aim of improving the mechanical, corrosion and tribological performance of NC surface layers. The present paper describes the process of fabrication of nanocrystalline Ni–Co/CoO functionally graded materials with significantly improved electrochemical corrosion and tribological performance; this involves the electrodeposition of nanocrystalline Ni–Co graded deposit and subsequent cyclic thermal oxidation to assemble a dry self-lubricating, corrosion and wear resistant top layer. To the best of our knowledge, this is the first report on such novel nanocrystalline deposits introducing the new concept of lubrication, wear and corrosion resistant functionally graded materials (lubricating and wear resistant graded materials; LGMs), which originally evolved from the application of functionally graded materials (FGMs) [9, 10].

2. Experimental procedures

2.1. Fabrication of nanocrystalline Ni–Co/CoO graded materials (Ni–Co/CoO LGMs)

NC Ni–Co alloys were electrodeposited on AISI-1045 steel substrates using a direct current electrodeposition method from a modified Watts-type electrolyte, containing nickel sulfate (200 g l^{-1}), sodium chloride (20 g l^{-1}), boric acid (30 g l^{-1}), sodium lauryl sulfate (0.1 g l^{-1}), cobalt sulfate ($0\text{--}80 \text{ g l}^{-1}$) and saccharin as a stress reliever and grain refinement agent. Functionally graded Ni–Co deposits (Ni–Co FGDs) were produced by varying the concentration of cobalt sulfate in the plating bath while keeping the current density at 3 A dm^{-2} for a bath temperature of 45°C as described in our previously published work [11]. Before deposition, the substrates were mechanically polished to a $0.10\text{--}0.12 \mu\text{m}$ (Ra) surface finish, then a sequence of cleanings was performed to remove contamination on the substrate surface, the steel substrates were activated for 20 s in a mixed acidic bath, then rinsed with distilled water. Then cyclic thermal oxidation and thermal quenching of NC Ni–Co graded deposits was carried out to obtain the NC Ni–Co/CoO graded materials with better lubricating and anti-wear properties (called Ni–Co/CoO LGMs). Preliminary experiments were conducted to establish the optimal oxidation temperature in terms of deposit strength and tribological properties. It was found that oxidation at 300°C did not cause loss of hardness or

phase transformation. The cyclic thermal oxidation–quenching process was as follows: the NC Ni–Co graded deposits were heated to 300°C in air for 20 min and then quenched in water at 20°C for 1 min before being returned to the furnace. This procedure was repeated 10 times in order to obtain a dense and protective oxide layer on the NC Ni–Co graded deposits.

2.2. Microstructure characterization

The cross-sectional surface morphology of NC Ni–Co graded deposits was investigated using a JSM-5600Lv scanning electron microscope (SEM). The composition of the NC Ni–Co graded deposits were determined with an energy dispersive x-ray spectroscopy (EDS) analysis tool attached to the SEM. The outer oxide layer on Ni–Co graded deposits was analysed using x-ray photoelectron spectroscopy (XPS). A PHI-5702 x-ray photoelectron spectrometer was used in this work operating with monochromatic Al $K\alpha$ radiation at a pass energy of 29.4 eV . After subtracting the background signal, the spectra were fitted using one or more Gaussian–Lorentzian peak shapes. The deconvoluted peaks were identified by reference to an XPS database. The crystal structure and phase composition of alloy deposits were studied by x-ray diffraction (XRD) using Cu $K\alpha$ radiation ($\lambda = 0.154 \text{ nm}$). The grain size of the nanocrystalline deposit was directly examined using a JEM-1200EX transmission electron microscope (TEM). Samples for TEM analysis were prepared by jet polishing using a 10% perchloric acid 15% acetic acid and 75% methanol electrolyte at a temperature of -15°C .

2.3. Evaluation of electrochemical corrosion resistance and tribological behaviour

The electrochemical measurements were carried out in a three-electrode cell. A steel plate coated with deposits was used as a working electrode. A platinum plate and saturated calomel electrode (SCE) were used as the counter and reference electrode, respectively. Measurements were performed in 10 wt% NaOH and 3.5 wt% NaCl solutions at a temperature of 20°C , using a CHI760B potentiostat/galvanostat system. Potentiodynamic anodic polarization curves were established and the corrosion potential (E_{corr}) and corrosion current density (i_{corr}) were determined using the Tafel extrapolation method. The linear polarization resistance was determined by performing linear sweep voltammetry (LSV) at a scanning rate of 0.1 mV s^{-1} within the range of $\pm 15 \text{ mV}$ around the open-circuit potential.

The friction and wear behaviour was tested on a reciprocating ball-on-disc UMT-2MT microtribometer tester (Center for Tribology, Inc., CA, USA) at room temperature with a relative humidity of 45–50% under dry sliding conditions. Figure 1 is a schematic illustration of the wear test performed on the electrodeposited surface; two-axis force sensors of electrical and mechanical design (strain-gauge type) for real friction coefficient measurement can measure simultaneously and independently a horizontal friction force and a vertical normal load. An AISI-52100 stainless steel ball (diameter 4 mm) was used as the friction counter body. All tests were performed under a constant normal load of 3 N and a sliding speed of 0.11 m s^{-1} . The friction coefficient and sliding time were recorded automatically and precisely