INSTITUTE OF PHYSICS PUBLISHING JOURNAL OF PHYSICS D: APPLIED PHYSICS

J. Phys. D: Appl. Phys. **38** (2005) 1318–1324 doi:10.1088/0022-3727/38/8/033

Graded composition and structure in nanocrystalline Ni–Co alloys for decreasing internal stress and improving tribological properties

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Received 3 July 2004, in final form 18 February 2005
Published 1 April 2005
Online at stacks.iop.org/JPhysD/38/1318

Abstract
In this paper, nanocrystalline Ni–Co alloys with continuously graded composition and structure were produced by the electrodeposition method. The internal stress of the graded Ni–Co nanocrystalline alloys generated during the electrocrystallization and the tribological properties were investigated and compared with Ni–Co alloys with a uniform structure. The results show that with continuous changes in composition and structure, the internal stress generated during the electrodeposition process was decreased to approximately the minimum level. Additionally, the graded Ni–Co nanocrystalline alloys exhibited a remarkably improved wear resistance and a much lower friction coefficient compared with the Ni–Co alloys with a uniform structure under the dry sliding wear conditions. And the graded Ni–Co nanocrystalline alloys retain perfect friction and wear properties as the annealing temperature increases up to 400˚C.

1. Introduction

Nanocrystalline metals produced by electrodeposition techniques have attracted intensive investigations for basic research as well as applied sciences [1–3]. To further extend the applications of nanocrystalline metals, the need for nanocrystalline alloys with high hardness was keenly felt. However, the growth of nanocrystalline alloy deposits during the electrocrystallization process was normally accompanied by the generation of a high internal stress [4, 5], which directly affects the properties of the deposits and may cause their cracking and peeling off from the substrates. This generally restricted their applications, especially for anti-corrosion and anti-wear purposes, with thicker deposits.

A possible approach to decreasing the internal stress of electrodeposited nanocrystalline alloys is to introduce the new concept of gradient materials. Previously studies have shown that gradient materials show interesting properties in the field of thermal, electrical and separation applications [6–8]. But a few studies have reported investigations on the friction and wear properties of gradient materials since friction and wear are of great concern, especially in industrial components, resulting in huge economic losses and sometimes catastrophic failure [9].

Ni–Co alloys have been investigated as important engineering materials for several decades because of their unique properties, such as high strength, good wear resistance, heat-conductivity, electrocatalytic activity and specific magnetic properties [10–14]. In this paper, graded Ni–Co nanocrystalline alloys were produced by electrodeposition, and the internal stress and tribological behaviour of graded Ni–Co alloys were investigated as compared with Ni–Co alloys with uniform structure.

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0022-3727/05/081318+07$30.00

2. Experimental procedures

2.1. Deposition of graded Ni–Co nanocrystalline alloys

Nanocrystalline (nc) Ni–Co alloys were electrodeposited on AISI-1045 steel substrates using the 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 ($0–80\,g\,l^{-1}$) and saccharin as a stress reliever and grain refinement agent. Graded Ni–Co alloys were produced by varying the concentration of cobalt sulfate in the plating bath while maintaining the current density at $3\,A\,dm^{-2}$ and a bath temperature of 45˚C. The anode was a pure Ni plate. The pH of the bath was maintained at 4.0, adjusted by ammonia water or dilute sulfuric acid. Before deposition, the substrates were mechanically polished to a 0.10–0.12 μm surface finish, and then a sequence of cleanings were performed to remove contamination on the substrate surface, and the steel substrates were activated for 20 s in a mixed acidic bath and then rinsed with distilled water. Then the alloy deposits were annealed at 100˚C, 200˚C, 300˚C and 400˚C in air, respectively, to investigate the effects of annealing temperature on the hardness and tribological properties of the deposits.

2.2. Compositions and structures

The surface morphology of nc Ni–Co alloys were investigated using a JSM-5600Lv scanning electron microscope (SEM). The composition of nc Ni–Co alloys were determined with an energy dispersive x-ray spectroscopy (EDS) analysis tool attached to the SEM. At different depths from the substrate, eight local points were chosen for measurement of the Ni and Co content. Finally, the depth profiling of the EDX data in the deposit was obtained by linking these average values, obtained at different thicknesses of deposits. The crystal structure and phase composition of the alloy deposits were studied by x-ray diffraction (XRD) using CuK_α radiation ($\lambda = 0.154$ nm). The grain size was estimated by applying the Bragg and Scherrer formula for XRD peak broadening to the (111) reflections, after correction for instrumental line broadening using a silicon standard [15, 16]. To verify the accuracy of the grain size measurements, some specimens were also examined in a JEM-1200EX transmission electron microscope (TEM). The microhardness of the alloy coatings was determined using a Vicker's microhardness indenter with a load of 50 g for 10 s, and indentations were made on 100 μm thick deposits. The final value quoted for the hardness of a deposit was the average of 10 measurements.

2.3. Internal stress measurement

The mean internal stress generated during electrodeposition was measured using a device based on the bent cathode method. A copper strip, insulated on one side, was held rigidly at one end; the development of internal stresses within the Ni–Co alloy deposits could bend the specimen, and the free end of copper strip was allowed to deflect. A compressive stress will bend the strip towards the insulated side, while a tensile stress will bend the strip towards the plated side as shown in figure 1. The average internal stress, σ, was determined by the measured displacement, z, of the plated part of the strip from the well known Stoney's equation, which was widely used for stress determination and presented in [17–19].

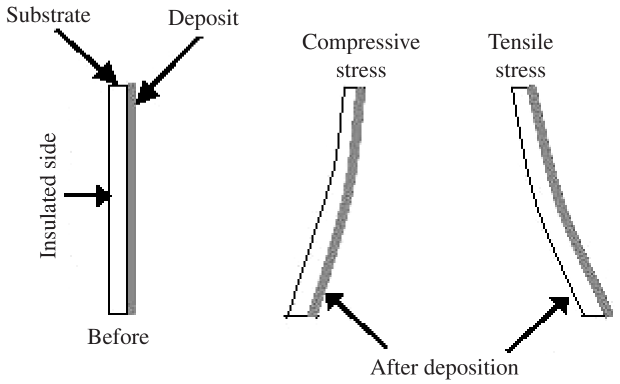

Figure 1. Schematic illustration of measurement of the internal stress in a deposit.

$$\sigma = \frac{Ez(t_s^2 + t_s t_d)}{3t_d L^2}, \quad (1)$$

where E, t_s, and L are the Young's modulus, the thickness and the length of the plated part of the copper strip, respectively; the values for the copper strip were $E = 1.1 \times 10^5$ MP, $t_s = 0.035$ mm and $L = 50$ mm. t_d is the total thickness of the deposit.

2.4. Friction and wear tests

The friction and wear behaviour was tested on a reciprocating ball-on-disc UMT-2MT tribometer tester (Center for Tribology, Inc., California, USA) at room temperature with a relative humidity of 45–50% under dry sliding conditions. AISI-52100 stainless steel ball (diameter 4 mm) was used as the counter body. The friction coefficient and sliding time were recorded automatically during the test. The wear volume was measured using a surface profilometer after the wear test; the wear rates of all the deposits were calculated using the equation $K = V/SF$, where V is the wear volume in mm^3, S is the total sliding distance in m and F is the normal load in N.

3. Results and discussion

3.1. Graded composition and structure

The typical surface morphology of graded Ni–Co nanocrystalline alloys is shown in figure 2. In general, the surface exhibited a flat and mirror-like appearance; under conventional SEM observations, the grain size of the deposits cannot be resolved. The distribution of Co content in the graded Ni–Co alloy deposits in the direction of the deposit thickness was shown in figure 3. It is evident that the composition gradually changes from the Ni-rich region to the Co-rich region as a function of distance from the interface, which is in accordance with the experimental design of Ni–Co gradient alloys. Based on the above results, it can be concluded that the continuously graded composition in the Ni–Co nanocrystalline alloys was obtained by simple control of the Co^{2+} concentration during the electrodeposition process.