Surface & Coatings Technology 271 (2015) 148–155

Contents lists available at ScienceDirect

Surface & Coatings Technology

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

Nanostructured gradient Co-Sn electrodeposits as alternative to Sn connector contacts

E.P. Georgiou [a,b,*], J.G. Buijnsters [c], H. Wang [a], D. Drees [b], A.K. Basak [d], J.-P. Celis [a]

[a] KU Leuven, Materials Engineering (MTM), Kasteelpark Arenberg 44, Leuven B-3001, Belgium
[b] Falex Tribology NV, Wingepark 23B, Rotselaar 3110, Belgium
[c] Department of Precision and Microsystems Engineering, Research Group of Micro and Nano Engineering, Delft University of Technology, Mekelweg 2, Delft 2628 CD, The Netherlands
[d] The university of Adelaide, South Australia, SA 5005, Australia

ARTICLE INFO

Available online 3 January 2015

Keywords:
Nanostructured
Gradient coatings
Electrodeposition
Microstructure
Wear

ABSTRACT

Gluconate plating baths were successfully used for the synthesis of homogenous, crack-free nanostructured gradient Co-Sn coatings. The grain size of electrodeposited Co-Sn sub-layers was found by X-ray Diffraction to range from 10 up to 143 nm, whereas the increase of Sn content into the Co-Sn sub-layers led to an increase of average grain size. The average hardness of the gradient coating was found to be significantly higher than that of the pure Sn electrocoating, due to the presence of intermetallic phases. In addition, the frictional properties of the Co-Sn gradient coatings strongly depend on the thickness of the pure Sn top layer, as the thin top layer can shear when sliding against the counterface material. On the other hand, thick Sn layers as in the case of pure Sn electrodeposits result in a higher coefficient of friction of the tribosystem due to adhesive wear phenomena, brought about by the formation of debris at the sliding contact. Furthermore, nanostructured gradient Co-Sn coatings are found to have significantly higher wear resistance when compared to pure Sn coatings. The main wear mechanisms observed were adhesive and abrasive wear of the Sn top layers and subsequent deformation and cracking of the intermetallic based Co-Sn sub-layers.

1. Introduction

Recent progress in thin-film deposition technologies has led to the synthesis of new generations of nanostructured, self-lubricating coatings with composite or multilayered structures, which progressively make their way into the commercial marketplace and meet the ever-increasing performance demands of more severe applications [1]. Physical vapor deposition (PVD) and chemical vapor deposition (CVD) are well-known methods for depositing such coatings [2]. However, the associated drawbacks such as size of deposition area, substrate geometry, cost, and complexity of the process often limit their usage. In this perspective, electrodeposition is a versatile and efficient technique, which can potentially be utilized for the synthesis of complex nanostructured coatings especially in industrial scale.

Among the various electrodeposited systems used up-to-date, Co-Sn electrocoatings are extensively applied as a convenient and economic way to achieve an attractive finish on lock and door hardware, plumbing fixtures, appliance components, office equipment, tools, computer electrical components, tubular furniture, store fixtures, jewelry, hinges, kitchen utensils, tubular furniture, and automobile interior trim and fittings [3]. In addition, Co-Sn alloy coatings have mechanical and electrochemical properties similar to those of chromium electrocoatings [4]. However, despite the industrial [5,6] and scientific [7–12] interest for Co-Sn alloy coatings, published data on the mechanical and tribological properties of such coatings are yet very limited. In addition, very little has been reported on the development of gradient Co-Sn multilayers. In particular, only one research report can be found on the electrodeposition composition modulated Co-Sn coatings [13]. The aim of this work was to study the electrodeposition and the fatigue properties of multilayered Co-Sn alloy coatings as possible overlays for plain bearings. However, nothing has been reported on the tribological characteristics of such coatings, as one of the main reasons of their failure is due to wear phenomena, e.g., contact connectors, aerospace bearings, etc.

Therefore, in this research novel nanostructured gradient Co-Sn coatings were deposited onto copper substrates via conventional direct current plating as potential alternatives for existing tin connector contacts. Single layered Sn coatings are considered as low cost and reliable alternatives to gold and silver plating. However, one of their main drawbacks is their susceptibility to fretting wear, which is mainly brought about by micro-motion movements (e.g. vibration and shock) and a

* Corresponding author at: KU Leuven, Materials Engineering (MTM), Kasteelpark Arenberg 44, Leuven B-3001, Belgium. Tel.: +32 16321292; fax: +32 16321991.
E-mail address: Emmanuel.Georgiou@mtm.kuleuven.be (E.P. Georgiou).

http://dx.doi.org/10.1016/j.surfcoat.2014.12.061
0257-8972/

build-up of oxide debris at the contacting interface. The amplitude of this fretting motion is observed to range between 10 and 200 μm [14] and can thus result either in a partial slip, mixed or gross slip fretting regime. In this work, the wear characteristics of the coatings are evaluated in gross slip regime, as Sn coatings are highly prone to adhesive wear and shearing under such conditions. On the other hand, nanostructured gradient Co-Sn coatings can provide an alternative, as they can combine the lubricating properties of a thin Sn layer with the mechanical and wear resistance of the intermetallic Co-Sn phases. In particular, the materials design for these gradient Co-Sn structures, as seen in Fig. 1, is based on the lubricating effect of a nanosized Sn top layer, the formation of Co-Sn intermetallic sub-layers to provide adequate load bearing capacity and a pure Co sub-layer at the interface to strengthen the adhesion of the gradient coating with the copper substrate.

This is the first research work report on the development of nanostructured gradient Co-Sn coatings, whereas the existing know-how on the production of gradient coatings by electrodeposition is still extremely limited. This work presents clear evidence that complex gradient coatings can indeed be synthesized by electrodeposition. In addition, nanostructured gradient Co-Sn coatings can be successfully used to replace Sn coatings, as they have improved frictional and wear characteristics.

2. Experimental procedure

The substrate material used was a commercially supplied copper sheet. Rectangular specimens with dimensions 4 cm × 2 cm × 0.1 cm were used. These flat specimens were mechanically polished with SiC papers and diamond pastes. The resulting roughness was approximately Ra 0.07 μm.

For the electrodeposition of the Co-Sn gradient coating and single sub-layers, adjusted gluconate aqueous baths were used. The electrodeposition parameters are given in Table 1. Bath agitation was done by a magnetic stirrer rotating at 400 rpm and located at the bottom of a 250 ml glass beaker used as plating cell. A flat graphite electrode with dimensions 4 cm × 2 cm × 0.5 cm was used as anode. The copper substrate and the graphite anode were placed vertically facing each other at a distance of 2 cm. The gradient structure was obtained after consecutive depositions from different gluconate baths, as indicated in Table 1.

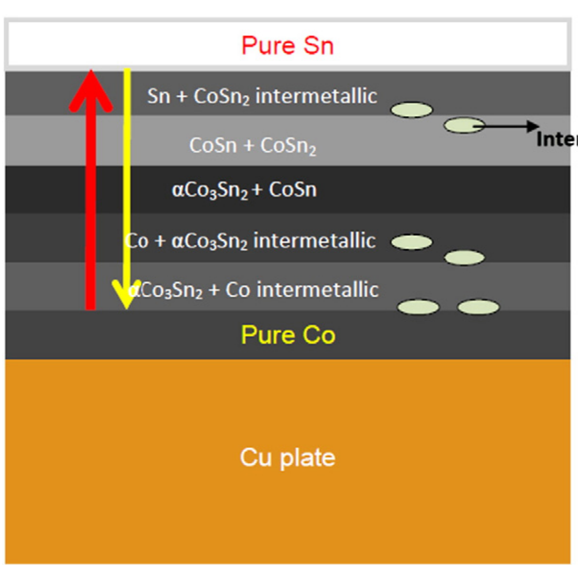

Fig. 1. Cross section of gradient Co-Sn coatings: material design approach.

Table 1
Plating parameters and bath composition for each sub-layer of gradient Co-Sn electrocoating.

Bath composition					Coating composition
Nr.	Cobalt(II) sulfate (g/L)	Tin(II) sulfate (g/L)	Gluconate (g/L)	Polyphosphate (g/L)	Sn content (at.%)
1	7	–	20	15	–
2	7	0.25	20	15	4.2
3	7	0.5	20	15	12.3
4	7	1	20	15	23
5	7	1.5	20	15	33
6	7	3	20	15	50
7	–	3	20	15	100

Deposition conditions: current density = 1 A/dm^2, temperature = 45 °C, Time = 5 min.

It should be noted that the plating parameters presented were selected alter preliminary testing and optimization of the plating process.

The surface morphology and chemical composition of the Co-Sn gradient coatings and sub-layers were analyzed in an FEI XL 30 FEG scanning electron microscope connected to an electron dispersive X-ray analyzer (EDS) apparatus. Cross sections and transmission electron microscopy (TEM) sample preparation were prepared by ion milling (Helios Nanolab 600 SEM/FIB). The crystallographic structure of the coatings was investigated by X-ray Diffraction (XRD) using a Seifert 3003 T/T machine with Cu K_a radiation The goniometer is equipped with a Cu tube. A generator of 1200 Watt (40 kV, 30 mA)

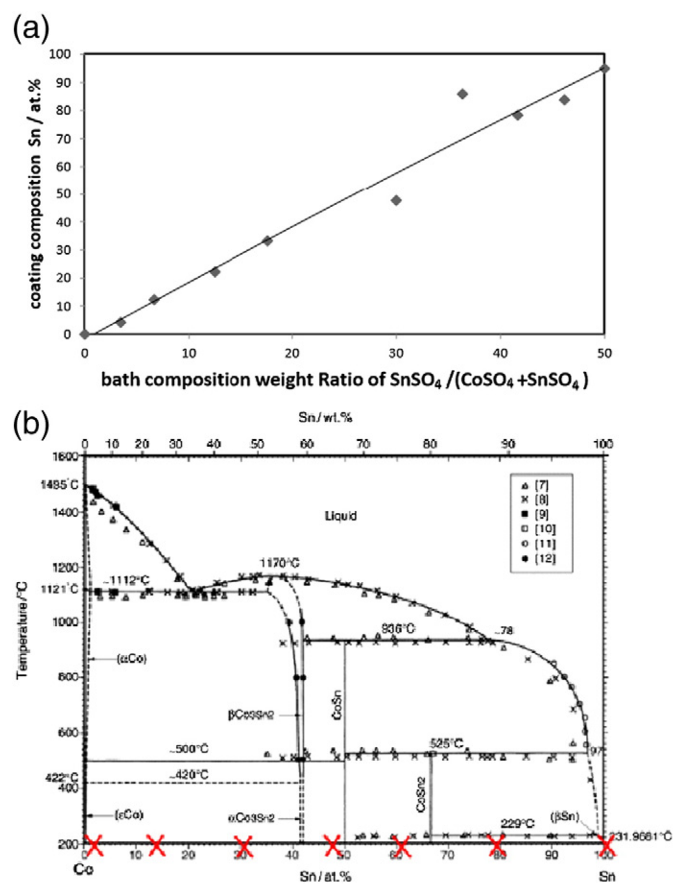

Fig. 2. (a) Effect of weight ratio of $SnSO_4/(CoSO_4 + SnSO_4)$ in the plating bath on the at.% of deposited Sn in the coating. (b) Co-Sn binary phase diagram. X indicates Co-Sn electrodeposited composition.