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TRIBOLOGICAL PERFORMANCE OF NANOSTRUCTURED INTERMETALLIC ELECTRODEPOSITS AT DIFFERENT LOAD-SCALES

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Abstract: *This works presents an overview of the tribological performance of various Ni and Co based electrodeposits under different contact conditions that relate to a field of applications. By applying meso-loads tests, the frictional and wear performance of thin nanostructured layers can be more realistically evaluated for micro-electronic systems (without overstressing the system and by minimizing substrate effect), whereas macro-loads can be used to simulate larger mechanical components. The key to this tribological approach is to simulate similar contact conditions and generate the same wear mechanisms as in the end-user application.*

Key words: *Electrodeposition; Ni-Sn; Co-Sn; Intermetallics; Nanostructured; Tribology; Meso-scale.*

1. INTRODUCTION

During the last decades there is an increasing interest and a rapid development of new nanostructured materials for industrial applications [1]. Indeed, up to date they have been successfully applied, either as coatings or bulk materials, in a wide range of technological fields ranging from micro-electronics to large mechanical components in the aviation industry [2]. The applicability of nanomaterials can be further extended by optimization of their microstructural features such as secondary phase distribution, layer thickness etc. [3]

In addition, materials consisted of intermetallic compounds have been the subject of significant research and development efforts over the past decades due to their special physical, chemical and/or mechanical properties [4]. It has been observed that such alloys can exhibit a high hardness, possess an increased mechanical strength, resist corrosion and oxidation and have good frictional and wear properties. In that respect, it seems that a combination of nanostructuring and inter-metallics could bring about a further improvement of these technological properties and thus it is not surprising that there is an increasing interest for nanostructured intermetallics as innovative coatings for demanding applications. Furthermore, it is believed that such coatings can be potentially used for the replacement of hard chrome, which has an extremely negative environmental impact due to the use of the carcinogenic hexavalent chromium during the plating process [5].

Having the above in mind, this work presents the development of novel nanostructured Ni-Sn and Co-Sn intermetallic electrodeposits. Depending on the Sn content and plating parameters, these nanocoatings can contain either a mixture of a solid solution with dispersed intermetallic phases or a bulk intermetallic phase [6-7]. This allows tailoring the microstructure according to the specifications of a particular application. To evaluate the applicability of these coatings for tribological purposes, sliding wear tests were performed under different contact conditions that relate to a field of applications. By applying meso-loads tests, the frictional and wear performance of these nanostructured layers can be more realistically evaluated for micro-electronic systems (without overstressing the system and by minimizing substrate effect), whereas macro-loads can be used to simulate larger mechanical components; see for example [8-10]. In each load scale the wear mechanisms were assessed. The main goal is to establish a structure-property relationship and to explore the future applicability for these materials.

2. EXPERIMENTAL

The substrate material used was a commercial Vanadis 23® steel (Uddelholm Corp.) containing 1.28 wt.% C, 4.2 wt.% Cr, 5 wt.% Mo, 6.4 wt.% W, 3.1 wt.% V and Fe balance. This alloy is a high-speed powder metallurgical steel, designed for demanding applications such as low-temperature die casting, warm forging and cutting tips, where strong emphasis is given on wear resistance. The reason for selecting this material as a substrate, was to have a strong reference point in terms of tribological properties. From the initial material flat parallel substrates having dimensions of 4 cm × 2 cm × 3 mm were produced. They were then mechanically ground with SiC papers and subsequently polished with 3 μm and 1 μm diamond pastes until the resulting roughness Ra was about 0.1 μm.

After mechanical preparation, the substrates were annealed in an argon inert furnace at 250°C for 2 h, so as to remove the residual stresses.Before the electrodeposition of Ni-Sn and Co-Sn coatings, a Ni strike layer was electrodeposited onto the steel substrates, to improve adhesion. The composition of the Ni strike plating bath was 100 g l^{-1} $NiCl_2*6H_2O$, with a pH of 1–1.5. The current density was 60 mA cm^{-2}, the electrodeposition time was 1 min, and the plating bath temperature was 25 ± 2 °C. A flat nickel electrode with dimensions 4 cm x 2 cm x 0.1 cm was used as anode. The electrodeposition process, path and parameters for the Ni-Sn and Co-Sn electrocoatings are described in our previous publications [6] and [7] respectively.

The microstructure and chemical composition of Ni-Sn coatings as-plated, and after exposure to 400 °C in ambient air, were analyzed in a FEI XL 30 FEG® microscope connected to an energy dispersive X-ray analyzer (EDS). Cross sections of as-plated samples were prepared by ion milling in a FEI NOVA 600 Nanolab® Dual Beam SEM/FIB, and then analyzed. The crystallographic structure was investigated using a Seifert 3003® T/T X-ray Diffractometer (XRD) with CuKa radiation. The hardness and Young's modulus of the test samples were determined by nanoindentation measurements with a Berkovich diamond indenter tip up to a normal load of 50 mN and reported as mean values calculated from 10 duplicated indentations.

The tribological behavior of the electrodeposits was evaluated under dry reciprocating sliding conditions, at meso- and macro-load scales. A microtribometer (Basalt N2®, Falex Tribology NV, Belgium) was used to perform reciprocating sliding tests at normal loads ranging from 40 mN up to 2.5 N. A displacement amplitude of 300 μm and a sliding frequency of 1 Hz were used. 100Cr6 balls with a diameter of 5 and 10 mm and a surface roughness Ra of 0.1 μm were used as counterface materials for the meso- and macro-load wear experiments respectively. Prior to the reciprocating sliding tests, the coated specimen and the counter-bodies were cleaned first with acetone and then alcohol to remove surface contaminants and dried. All reciprocating sliding tests were performed three times from which the mean values were calculated and presented in the graphs. The Hertzian contact pressures were calculated with HertzWin software. The obtained wear mechanisms were analysed in the SEM microscope and the wear was quantified with a 3D confocal microscope.

3. RESULTS AND DISCUSSION

SEM analysis of the electrodeposited coatings showed that a uniform thickness was achieved and neither cracks nor flaws were observed at the interface between the Ni strike layer and steel substrate or between the Ni strike layer and the electrodeposited layer, Figure 1. This is an indication of satisfactory adhesion between the electrodeposited layer, the Ni strike and the substrate. For the selected plating conditions, the maximum thickness was obtained for 80 min, see Figure 1a. Above that duration, localized cracks are formed due to hydrogen diffusion [11], see Figure 1b.

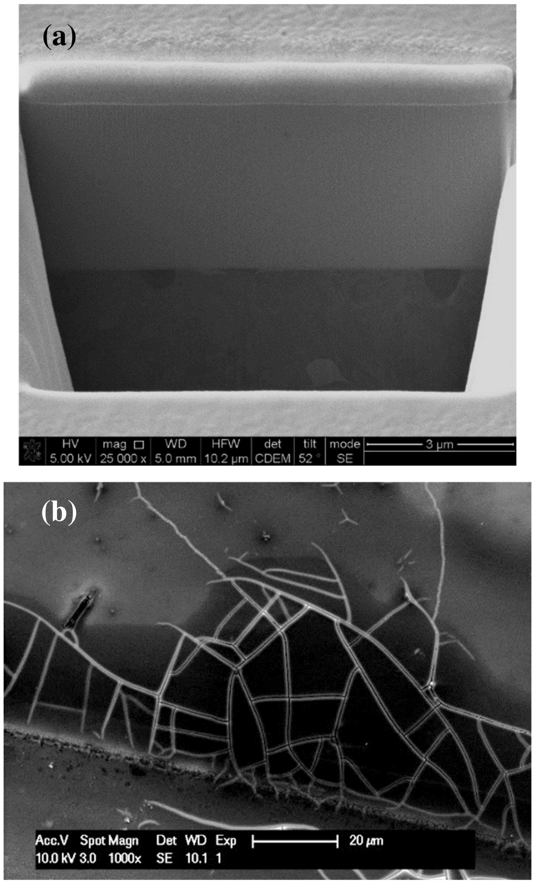

Fig. 1. (a) Indicative cross section of an electrodeposited Ni-Sn coating. (b) Formation of localized cracks due to hydrogen evolution during Ni-Sn electrodeposition.

By changing the concentration of tin within the plating bath, different rations of Ni/Sn and Co/Sn were obtained [6-7].

XRD analysis of the electrodeposits showed that in the case of Co-Sn a Co solid solution and Sn peaks were observed; see Figure 2a, whereas in for Ni-Sn electrodeposits a mixture of Ni solid solution and intermetallics; see Figure 2b and/or bulk intermetallics; see Figure 2c was obtained. The as-plated structures do not correspond to the expected from the binary Ni–Sn equilibrium phase diagram as the as the nucleation and growth of the deposited crystallites take place under non-equilibrium conditions as explained by electrocrystallisation mechanisms [12]. However, by performing post heat treatments there is the possibility to shift to equilibrium.

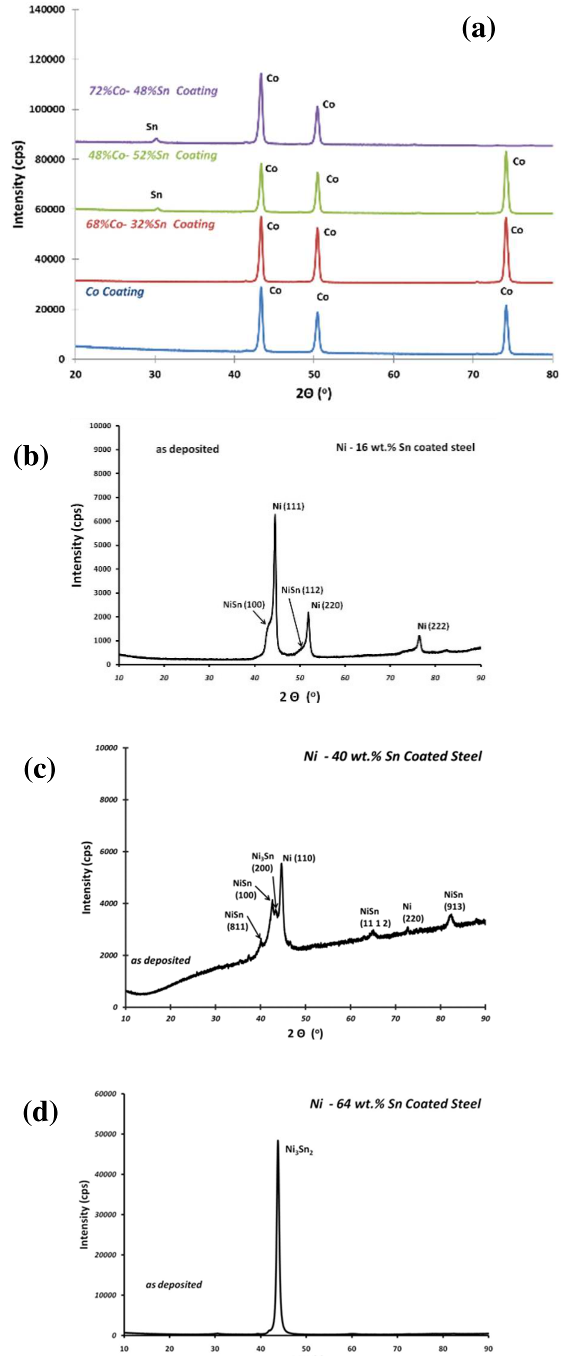

Fig. 2. X-ray diffraction of as-plated (a) Co-Sn and (b, c,d) Ni-Sn electrodeposits having different Sn content.

By changing the Sn content within the electrodeposits and by changing their microstructural features, their properties can be optimized according to the application. An example is given in Figure 3, were Sn concentrations around 60 wt.% seem to bring about the highest nano-hardness. This is due to the fact the in that range of concentrations, bulk intermetallics are obtained; see Figure 2c.

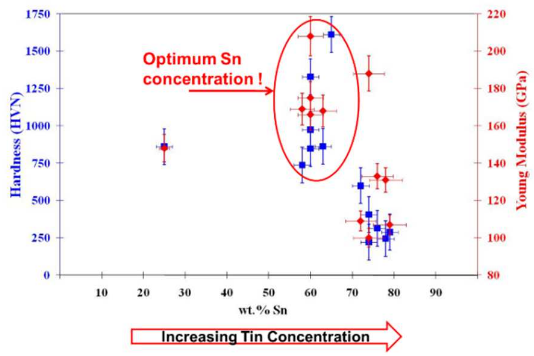

Fig. 3. Effect of Sn content on the nano-harness of Ni-Sn electrodeposits.

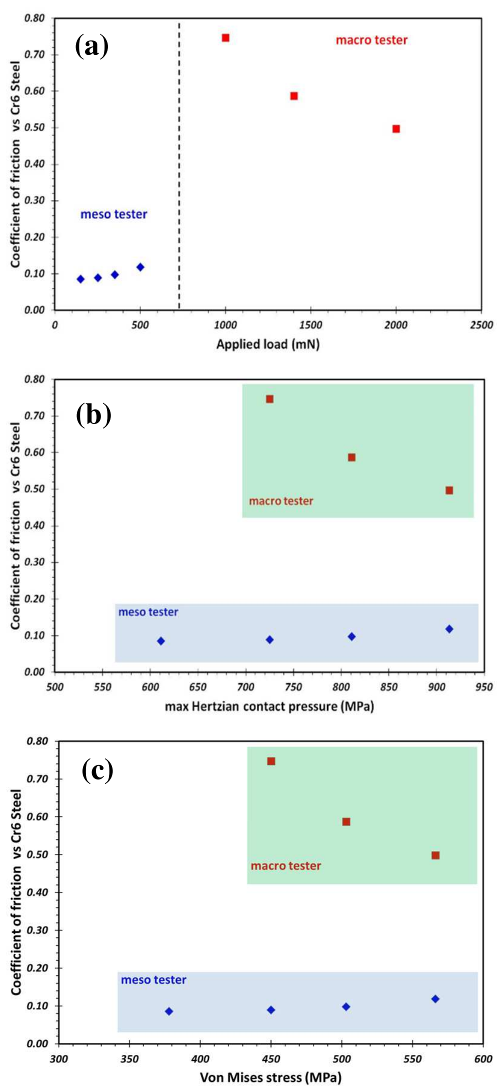

Fig. 4. Effect of (a) applied load, initial (b) Hertzian contact pressure and (c) Von Mises stress on steady state friction.

The tribological measurements on the meso- and macro-loads showed a completely different behaviour in terms of friction, Figure 4a. Even when the calculated contact pressures were the same, a significant difference in friction was observed. To understand this behaviour, SEM analysis of the wear tracks was performed.

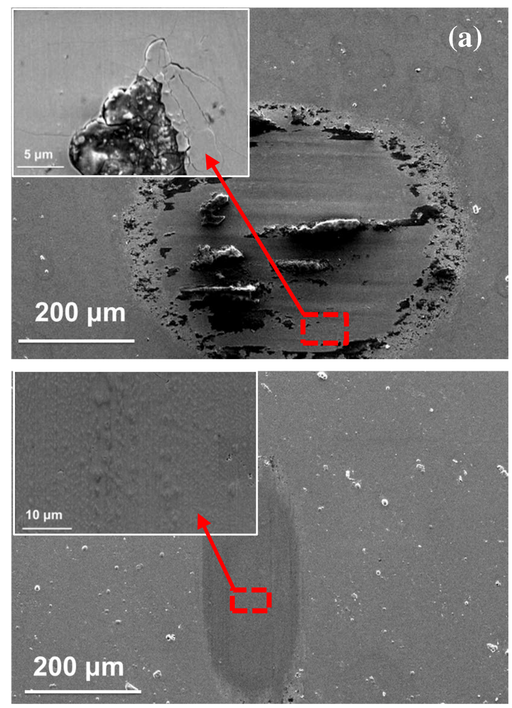

Fig. 5. SEM wear track analysis on Ni-Sn electrodeposit obtained after (a) macro- and (b) meso-load tests for the same Hertzian contact pressure (810 MPa)

Indeed, the morphology obtained after the macro- and meso-load tests; see Figure 5, appear to be very different, as in the case of meso-load tests mild abrasion and localized adhesion phenomena are observed, whereas for the macro-load tests a mixture of 2-body and 3-body abrasion (due to debris formation), along with adhesive and extensive cracking are evident. This finding demonstrates that conventional macro-load scale wear testers are not suitable for studying the wear behavior of thin layers containing brittle intermetallic phases. This is because the high initial contact pressure results in severe deformation and/or fracturing of the coating takes place instead of a moderate wear mechanism. Meso-load testing is a useful tool, as it allows to record accurately the frictional behavior of a thin or brittle coating without destroying it by mechanical load.

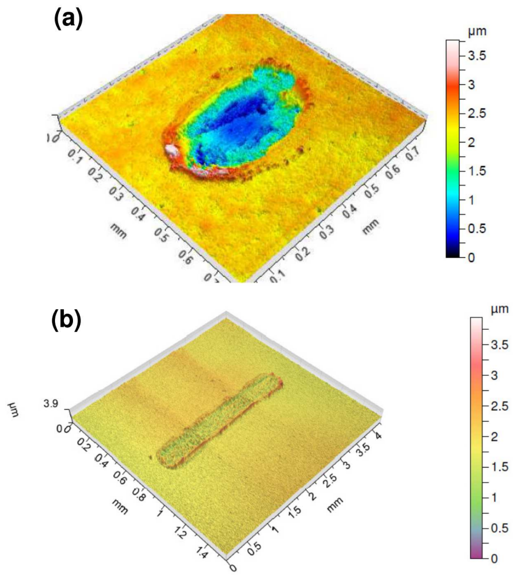

Fig. 6. 3D Confocal analysis of wear tracks on Ni-Sn electrodeposit obtained after (a) macro- and (b) meso-load tests for the same Hertzian contact pressure (810 MPa)

To quantify the wear damage, 3D Confocal analysis of the wear tracks was performed (Figure 6). These images confirm that with high load testing, despite having a similar contact pressure, the interaction volume is higher and severe deformation occurs, resulting rupturing of the coating. In addition, it should be mentioned that for thin layers, the greater the load the higher the substrate effect is and thus the risk of crack generation at the interface, especially when the coating has different mechanical characteristics from the substrate.

Finally, the concentration of Sn within the coating played a significant role in the frictional performance of the tribo-system at the meso-load scale. Higher Sn concentrations led to increased generation of Sn based debris within the tribo-contact and to the formation of clusters as shown in Figure 7a. This phenomenon can result in adhesive wear [7], as the debris particles may transfer onto the inert counter-material and change the tribo-chemistry of the system, shifting it from oxide versus metal to metal-metal contact (tin against tin). This hypothesis was supported by the evolution of sliding loops during a meso-load test, where a decrease of sliding displacement along with higher friction forces indicated the presence of sticking phenomena, see Figure 7b.

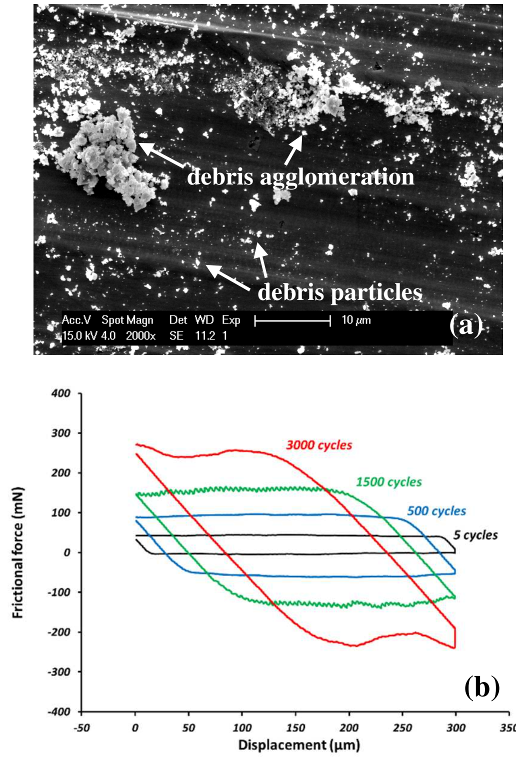

Fig. 7. (a) Formation of debris clusters within the tribo-contact, observed on the surface of Ni-64%Sn electrodeposit after meso-load testing at 810 MPa. (b) Evolution of sliding loops in a high Sn electrodeposit.

4. CONCLUSION

From this work the following conclusions can be drawn:

- Meso-load testers evaluate efficiently and accurately the frictional behaviour of nanostructured coatings.
- Severe deformation and/or fracturing of the coating in macro-load tester affect the coefficient of friction compared to the one measured with meso-load tester where neither deformation nor cracking is induced.
- Sn concentration played a significant role in tribological performance of boh Co-Sn and N-Sn electrodeposits, as it altered the wear mechanisms.

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Performance tribologique des dépôts électrolytiques intermétalliques nanostructurés à différentes échelles de charge

Résumé*: Ce travail présente un aperçu de la performance tribologique de divers dépôts électrolytiques à base de Ni et Co sous différentes conditions de contact se rapportant à un domaine d'applications. En appliquant des tests à charges moyennes, la performance en friction et en usure de fines couches nanostructurées peut être évaluée de manière plus réaliste pour les systèmes microélectroniques (sans surcharger le système et en minimisant l'effet du substrat), tandis que les charges macro peuvent être utilisées pour simuler des composants mécaniques plus grands. La clé de cette approche tribologique est de simuler des conditions de contact similaires et de générer les mêmes mécanismes d'usure que dans l'application finale.*

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