Tribological evaluation of multilayer coatings for wear applications based on a novel multiple scratch test method

M. Anand*, G. Burmistroviene, I. Tudela, R. Verbickas, G. Lowman, Y. Zhang

Daido Metal Co. Ltd, European Technical Centre (UK)
Research & Development Division
Winterhay Lane, Ilminster, TA19 9PH, United Kingdom

*Corresponding author: Dr Mayank Anand (Mayank.Anand@daidometal.com)

Abstract

A novel multiple scratch test method was developed for characterising the tribological performance of three different soft tin (Sn) based coating structures. Monolayer coating structure with soft Sn matrix, and 3-layers and 5-layers multilayer coating structures with soft Sn matrix and hard SnNi intermetallic sublayer (s) were produced by electroplating process. Experiments were carried out under various loading conditions and scratching the same coated surface by a 100Cr6 steel ball 50 times in a unidirectional cyclic manner. Load of 10 N allowed each scratch to remove the coating layer-by-layer and thus differentiating the characteristic friction and wear behaviours of three different coating structures. Multiple scratch test method also eliminated the influence of surface roughness of coating and hardness of substrate on tribological results. Post-test surface and cross-sectional analysis of scratched coatings showed the beneficial effects of the lubricious intermetallic sublayer within 3-layers and 5-layers multilayer Sn coating structures. The improvement in performance was even higher with lesser thickness of sublayers in 5-layers structure. In addition, scratch hardness and Vickers hardness measurements also demonstrated the increment in resistance to abrasive wear by the presence of intermetallic sublayer.

Keywords: Multiple scratch test method, Multilayer coatings, Friction, Wear, Scratch Hardness.

1. INTRODUCTION

Tribological applications in an internal combustion engine need high performing materials due to increasing firing pressures in combustion chamber for higher fuel efficiency and reduced emissions. In view of such a necessity, authors in past, proposed the multilayer Sn based coating to overcome the structural weaknesses of monolayer Sn based coating [1]. They demonstrated that the inclusion of SnNi intermetallic sublayer within Sn coating led to a significant improvement in the tribological performances [1-4]. The thickness of the coating is an important parameter that influences the performance of tribological contact [5]. It was envisaged that reducing the coating layer spacing by increasing the number of sublayers could also lead to better mechanical properties of a Sn based coating. Such development in multilayer coatings accounts for better understanding of their wear and abrasion behaviour [6].

The scratch test has been used by many researchers to assess the adhesion strength of hard coatings [7-11]. In order to evaluate the tribological performance of multi-layered soft coatings like Sn based, a single pass scratch test using either constant or progressive loading approach is not sufficient. At lower loads the influence of surface roughness of coating and at higher loads the effects of substrate hardness on friction and wear results is noticeable. Moreover, both of these approaches do not capture the effects of individual sublayers in a multilayer coating structure.

In the current research, a novel multiple scratch test method was developed for characterising the tribological performance of three different tin (Sn) based coating structures with and without intermetallic sublayer produced by electroplating process. The multiple scratch test method involves scratching the same coated surface multiple times in a unidirectional cyclic manner. This approach eliminates the influence of surface roughness of coating during the initial few scratches due to flattening of asperities and subsequently allowing the counterpart ball to slide onto relatively smoother surface. Each scratch removes the soft coating layer-by-layer thus allowing capturing of lubricious effects of SnNi intermetallic sublayer. Also the use of lower load helps avoiding the influence of substrate hardness on tribological results.

Experiments were carried out under various loading conditions to find the correct loading condition that can differentiate between the characteristic friction and wear behaviours of three different coating structures. Post-test surface and cross-sectional analysis to understand the wear mechanisms and change in microstructure of coatings were performed. In addition, scratch hardness and Vickers hardness of the coatings were also quantified since these parameters are good indicators of abrasion wear resistance [6].

2. EXPERIMENTAL DETAILS

2.1 Materials

100Cr6 steel ball (diameter = 6.35 mm) was used for scratching the flat coupon (L 50 x W 50 x T 5.2 mm) made of a lead-free bronze substrate electroplated with 20 ± 3 µm of Sn based coating and 2-3 µm of Ni based anti-diffusion barrier layer at the interface. Monolayer (1-layer), Multilayer 1 (3-layers) and Multilayer 2 (5-layers) structures of Sn based coatings were produced following the electroplating procedure as described in authors previous work [1-3]. The friction and wear performances of of the later two coating structures were compared against the benchmark Monolayer structure. Figure 1 shows the layer structures of the three coatings been investigated in the current study.

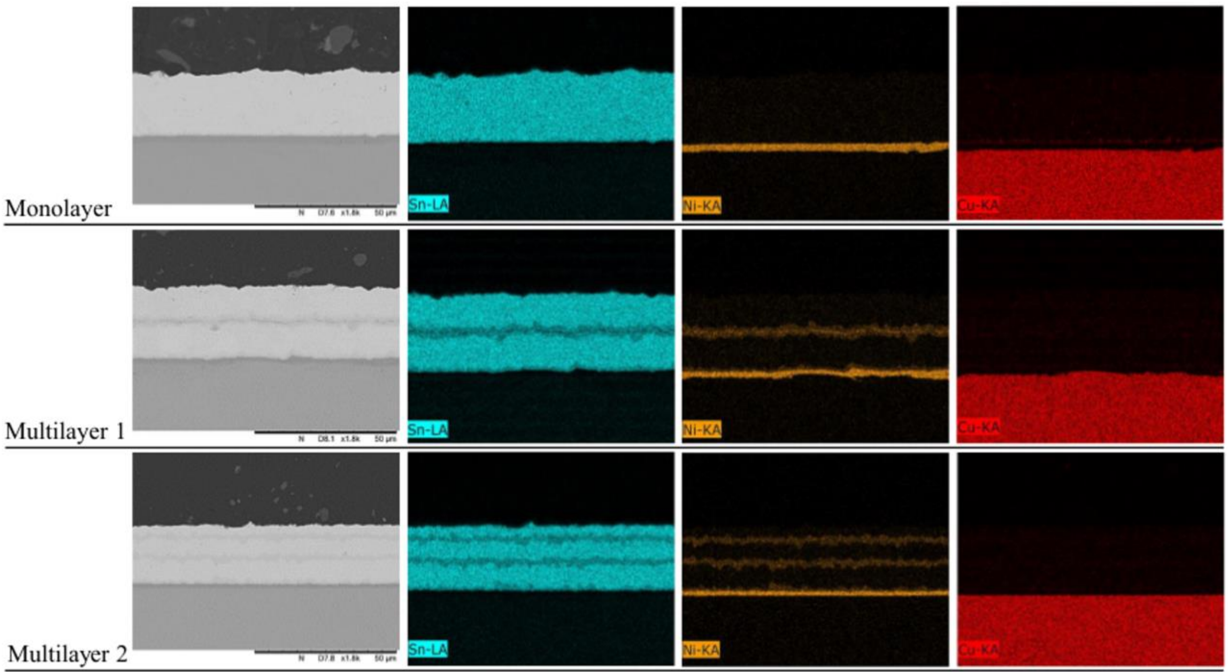

***Figure 1**: Cross-section of Sn based coatings; SEM micrographs and EDX elemental maps of Sn, Ni and Cu at 1800x magnification before test.*

2.2 Multiple scratch testing methodology

Unidirectional multiple scratch tests were performed using the scratch test module of Bruker's CETR Universal Materials Tester (UTM-2). Test parameters were input in the CETR UMT software and post test friction data was analysed using the CETR Data Viewer version 2.20 software. The schematic of the test setup is shown in Figure 2.

A ball probe attached to a suspension system (with maximum load carrying capacity of 200 N) is mounted onto a dual friction/load sensor. The loading range for the experiments was selected within the capacity of the dual load sensor and also to produce reproducible friction data. A flat coupon was mounted onto the base of elevated temperature chamber attached on top of the lower drive. The carriage moved in z-axis and pressed the ball against the coated flat coupon thus maintaining the prescribed load through a servo-controlled system. The slider then moved in x-axis and coating was scratched by the ball in the direction as shown in Figure 2. When the multiple scratch test was completed, the lower drive relocated the ball probe to a fresh surface for next test.

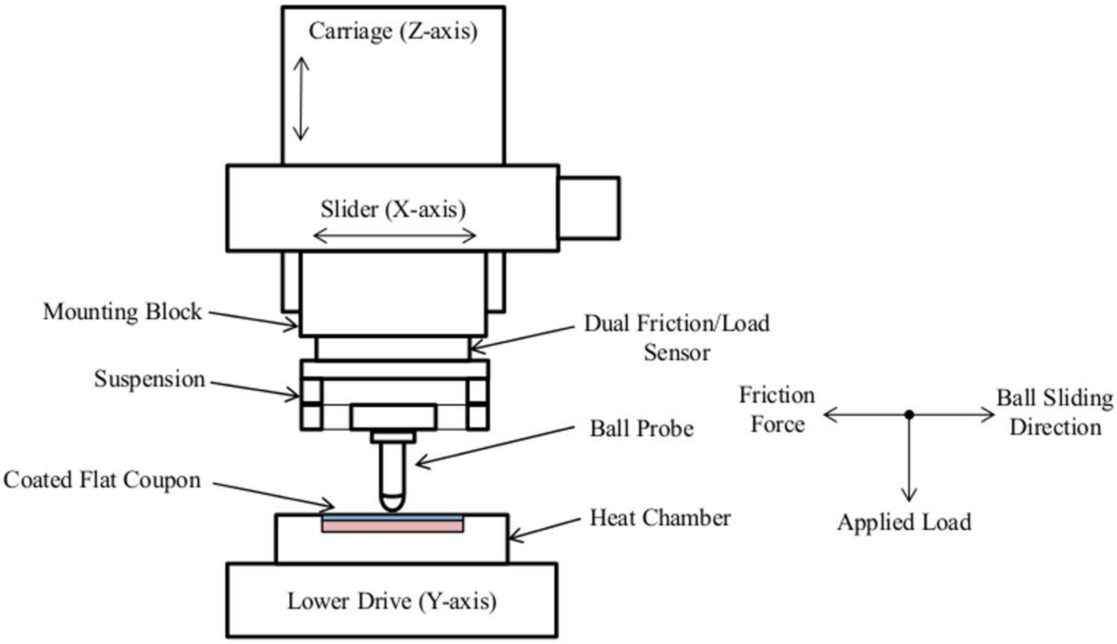

***Figure 2**: Schematic of Scratch test module of UMT-2.*

At the beginning of scratch test, a preload of 0.2 N was used to make the initial contact between the ball and the coupon. The static normal force was continuously increased until the maximum load was reached. The ball probe then scratch the coated surface while maintaining the constant maximum load. At the end of the scratch, the probe was raised by 3 mm and returned back to its initial position. The process was repeated 50 times and the tangential (friction) force was measured during each scratch cycle.

The different constant loads of 10, 30, 60, 90 and 120 N were used. The sliding speed was 0.167 mm/s and scratch length was 10 mm. The back temperature of the coupon was 130 ± 1 °C. The ambient temperature and relative humidity were 20 ± 2 °C and 30 ± 5 %, respectively. At the beginning of each test, 2 mL of SAE 20 synthetic base oil was applied onto the coupon surface to carry out testing in a lubricated mode. The lubricant used has a kinematic viscosity of 43.8 and 8.3 cSt at 40 and 100 °C, and contains only primary antioxidants which do not produce surface film, thus eliminates the effects of tribochemistry.

2.3 Material characterisation

The surface of each coating after scratch test was inspected using the Scanning Electron Microscope (SEM) for understanding the wear mechanism that existed during the scratching process. The cross-sectional microstructure and elemental distribution both before and after the scratch test were also studied. The equipment used for investigation was Hitachi TM3030 Plus at an accelerating voltage of 15 keV equipped with an Energy Dispersive X-ray (EDX) spectrometer.

The micro hardness of the coatings was measured on fresh surface using a Vickers hardness tester (Mitutoyo MicroWizhard HM221). Applied load for hardness measurement was carefully selected after various trials to avoid the infuence of surface roughness while measuring the average diagonal length of diamond indent left behind. Indentation was performed for a hold period of 10 s at the peak load of 30 gf. Each measurement was repeated five times and an average value was considered for analysis.

The depth at the middle of scratch (across the sliding direction) was also measured after each scratch test using a stylus based surface profiler (Taylor Hobson, Form Talysurf 120) for wear analysis. The data was analysed using the profile explorer software.

3. RESULTS & DISCUSSION

3.1 Friction behaviour

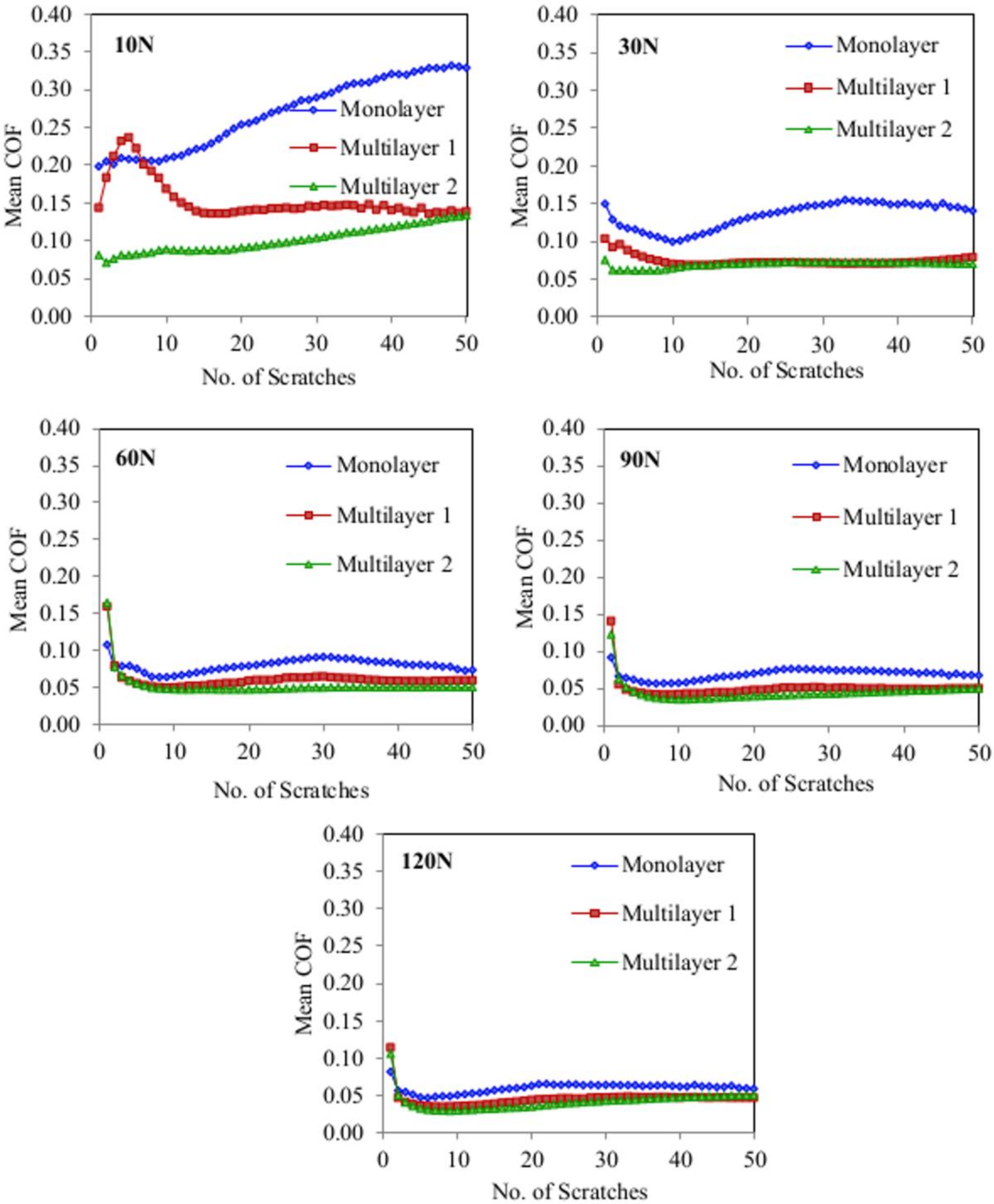

Figure 3: *Mean COF as function of multiple scratch cycles at different applied loads.*

Figure 3 shows a comparison between the friction performance of three structures of Sn based coatings as function of multiple scratch cycles (number of scratches). From the previous experience and reference to the published literature [1], it was hypothesied that the multilayer structure of soft Sn based electroplated coating on hard lead-free bronze substrate may potentially result in better friction properties than monolayer structure. However, to investigate the effect of layer structures with and without intermetallic sublayer on pure sliding friction, the experiments were carried out at a range of loads to find the most suitable loading condition to avoid the influence of substrate's hardness. The mean friction coeffcient (Mean COF) results, shown in Figure 3, are the average of two test results for each scratch cycle.

Clearly at higher loads, i.e. 60, 90 and 120 N, the subsrate effect is strong after only five scratches and all the three coatings follow a similar trend as friction becomes stable. Moreover, at 30 N, the friction values for Monolayer is a little elevated than that observed at other higher loads, but it also follows a similar trend.

10 N of applied normal load was found sufficiently low enough to avoid the influence of subtrate on friction behaviour to a higher degree. The difference in friction performance of three coatings is clearly visible. Multilayer 2 showed superior anti-friction performance, followed by Multilayer 1 and Monolayer being the least performing. It can be explained on the basis of different layer structures of Sn based coatings being studied.

The top intermetallic sublayer in Multilayer 2 coating is much closer to the surface and possesses excellent anti-friction propoerties, as explained by the authors in their pervious work [1]. Such intermetallic sublayer was formed at the interface between the Sn and Ni by thermal annealing after electroplating. Therefore, the friction was lowest in this case and only increased very gradually with the increasing number of scratch cycles.

Multilayer 1 also has this sublayer but at the middle of the coating structure. The possible explanation for the bump in friction curve within the first 15 scratch cycles for Multilayer 1 could be as follows. The increase in friction between the scratch cycles 1 to 5 was due to an increase in resistance to plastic deformation of top Sn sublayer by the underneath hard intermetallic sublayer as the sliding ball probe penetrates deeper. The reduction in friction between the scratch cycles 6 to 15 shows the lubricious effect of intermetallic sublayer when ball slides over it and then remained stable for the rest of the test.

On the other hand, Monolayer which has no such intermetalic sublayer showed reasonable frictional behavior, although it is not as good as multilayer structures. The friction results were stable till first 9 scratches and then showed a steady increase in a quasi-static manner for the remaining scratch cycles.

3.2 Wear behaviour

The depth at the middle of scratch (across the sliding direction) was measured from the surface after the completion of 50 scratch cycles using the surface profiler. Mean of two scratch depth values was taken for each coating tested at various loading conditions, and the error bar were used for postive and negative variations, as shown in Figure 4.

Clearly a trend showing an increase in the plastic deformation of the coatings with an increase in applied load can be seen. At 60, 90 and 120 N, the coatings were completely removed and the counterpart ball was sliding on either anti-diffusion layer or substrate. 30 N load produced slightly less wear than the higher loads, however, a minimal amount of coating was left such that the infuence of substrate was unavoidable. At lowest load of 10 N, almost half of the coating was remaining thus distinguishing clearly between the antiwear performance of three coating structures.

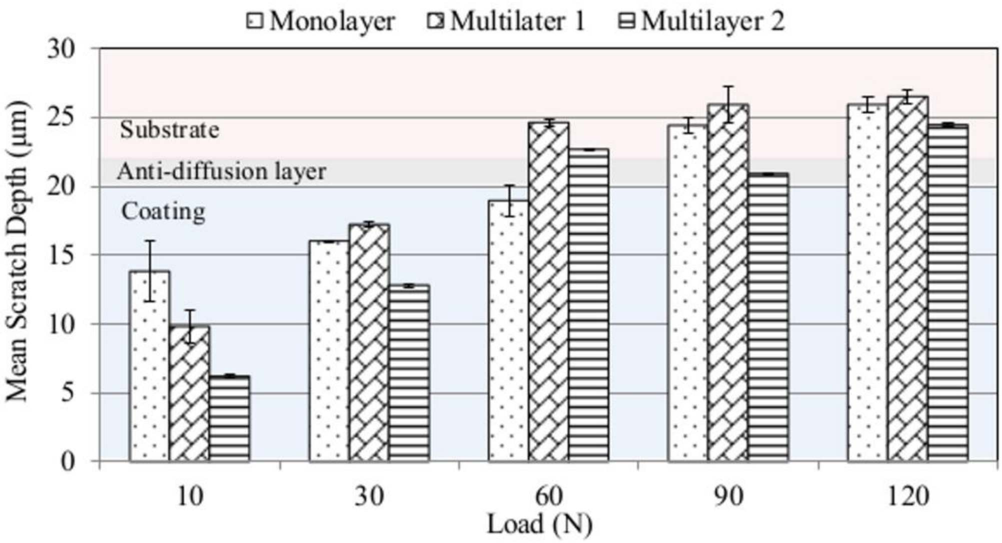

Figure 4: *Mean scratch depth at the middle of scratch after 50 scratch cycles.*

Figure 5 shows the evolution of wear as function of multiple scratch cycles at 10 N load, where the scratch depth was measured after certain number of scratches. In case of Monolayer, 32 % of total wear takes place in the first scratch after which the effect of loading stress reduces as the contact pressure decreases with an increase in contact area for the subsequent scratch cycles. It was also observed that after 30 scratches the scratch depth becomes almost stable. On the other hand, 29 % and 21 % of total wear was observed after the first scratch in case of Multilayer 1 and Multilayer 2, respectively. At the end of 50 scratches, the improvement in the wear resistance was 29 % and 54 % for Multilayer 1 and Multilayer 2, respectively, in comparison to Monolayer coating structure.

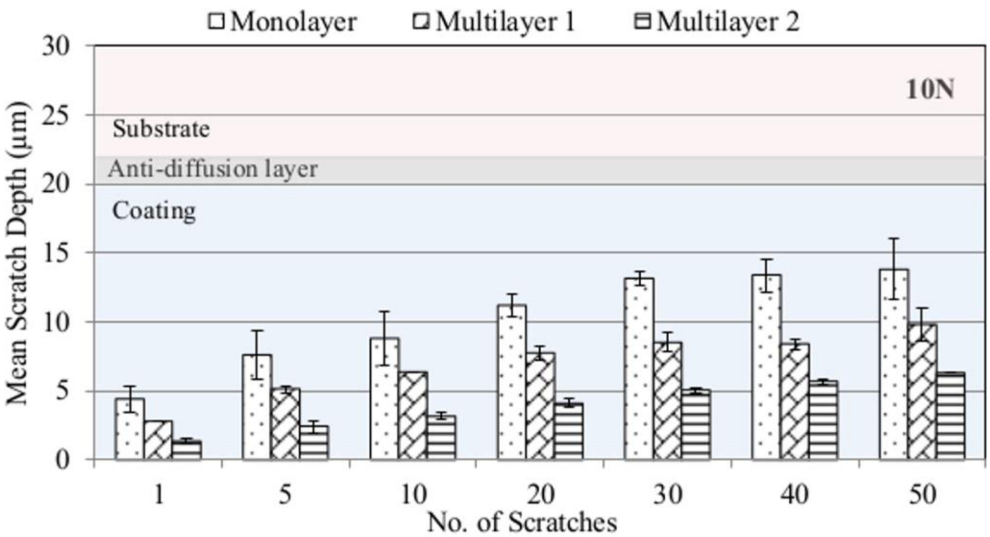

Figure 5: *Mean scratch depth at the middle of scratch as function of scratch cycles at 10 N.*

Although the overall trend in wear depth for all three coatings matches closely with the friction results for 10 N load (Figure 3), however, the wear results showed no symmetry to their friction counterpart in the first 15 scratches for Multilayer 1. This observation indicate that friction and wear are not directly related as explained by Blau in [12]. The processes that lead to friction and wear may arise from different material and systems properties and often do not reach steady-state at the same time [13,14].

3.4 Scratch Hardness

The scratch hardness to measure the materials resistance to scratch deformation can be given by the following equation [6,15].

$$H = \frac{F_n}{A} \qquad \text{(Eq 1)}$$

Where H is scratch hardness (N/mm^2) , F_n is applied load (N) and A is projected load-supporting area (mm^2). The scratch hardness has been used by researchers in past by incorporating the effect of the tip geometry and also geometric coeffecient [6]. Therefore the above equation can be re-written as:

$$H = x\,\frac{4}{\pi}\,\frac{F_n}{w^2} \qquad \text{(Eq 2)}$$

Where w is the remaining scratch width and x is the parameter with value of 2 assuming a pure plastic contact in the current study [15].

Table 1 suggests that the Multilayer 1 and Multilayer 2 coatings are 32 % and 57 %, respectively, more resistant to scratch deformation (or abrasive wear) than Monolayer. To verify the results of scratch hardness, the Vickers hardness of the three coatings was also measured at the fresh surface. The measurements were repeated five times and mean was considered. The results shown in Figure 6 also indicate a similar difference in the hardness of coatings. Since the intermetallic sublayer exhibits much higher hardness than Sn sublayer [1] and its position in Multilayer 2 is much closer to the surface than Multilayer 1, therefore, the wear resistance of Multilayer 2 is higher than Multilayer 1, followed by Monolayer which has no such sublayer in its structure.

Table 1: *Scratch width (mm) after multiple scartch test at 10 N.*

	Mean Scratch Width (mm)	Std. Dev.	Scratch Hardness (N/mm^2)
Monolayer	1.025	0.000	24.250
Multilayer 1	0.845	0.085	35.682
Multilayer 2	0.675	0.005	55.918

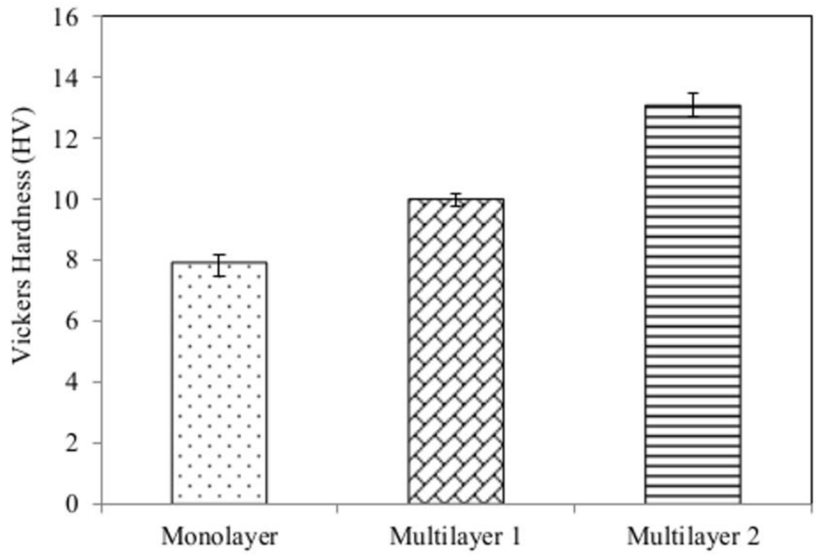

Figure 6: *Mean scratch depth at the middle of scratch as function of scratch cycles at 10 N.*

3.5 Wear mechanisms

SEM micrographs and EDX mapping of the scratched surface after 50 scratch cycles for the three coatings tested at 10 N are shown in Figure 7. The Monolayer has undergone the highest level of wear in terms of the scratch width. The surface morphology of Monolayer coating (at 1500x) depicts smoothing of asperities and accumulation of plastic flow of Sn coating on sides of the scratch leading to the formation of ridges [16, 17]. Such deformation phenomenon takes place when the hard steel ball plough through the soft coating, like Sn, and removes the material layer-by-layer with an increasing number of scratches. The steel ball penetrates deeper and gradually experiences the resistance to scratch deformation as it approaches towards the hard anti-diffusion layer (270 HV [1]). In addition, some mild abrasive wear lines on the scratched surface in the sliding direction was also obersved. Such wear mode can be attributed to the debris generated during sliding and get entrapped between the ball and coating surface causing micro-ploughing by 2-body abrasion.

On the other hand, the presence of an intermetallic sublayer in Multilayer 1 and Multilayer 2, has significantly reduced the wear. The surface morphology of worn region inside the scratch for these two coatings is different from that observed in Monolayer. The hard-soft interface between intermetallic sublayer (560 HV [1]) and Sn sublayer (15 HV [1]) in both Multilayer 1 and Multilayer 2 act as a barrier blocking the glide phenomenon of multiple dislocations in the top Sn sublayer. Thus making the multilayer structure less ductile compare to Monolayer. With the continous sliding, the pile-up of such dislocations takes place at the interface, as shown in Figure 7. The work hardening of the piled-up Sn under the mechanical loading results in strengthening of the multilayer structure [1, 18]. During the dislocations pile-up process, a part of the energy given to the tribosystem (either through sliding motion or applied normal load) is envisaged to be released as frictional energy which could explain the increment in Mean COF in first 5 scratches for Multilayer 1 (Figure 3, 10N).

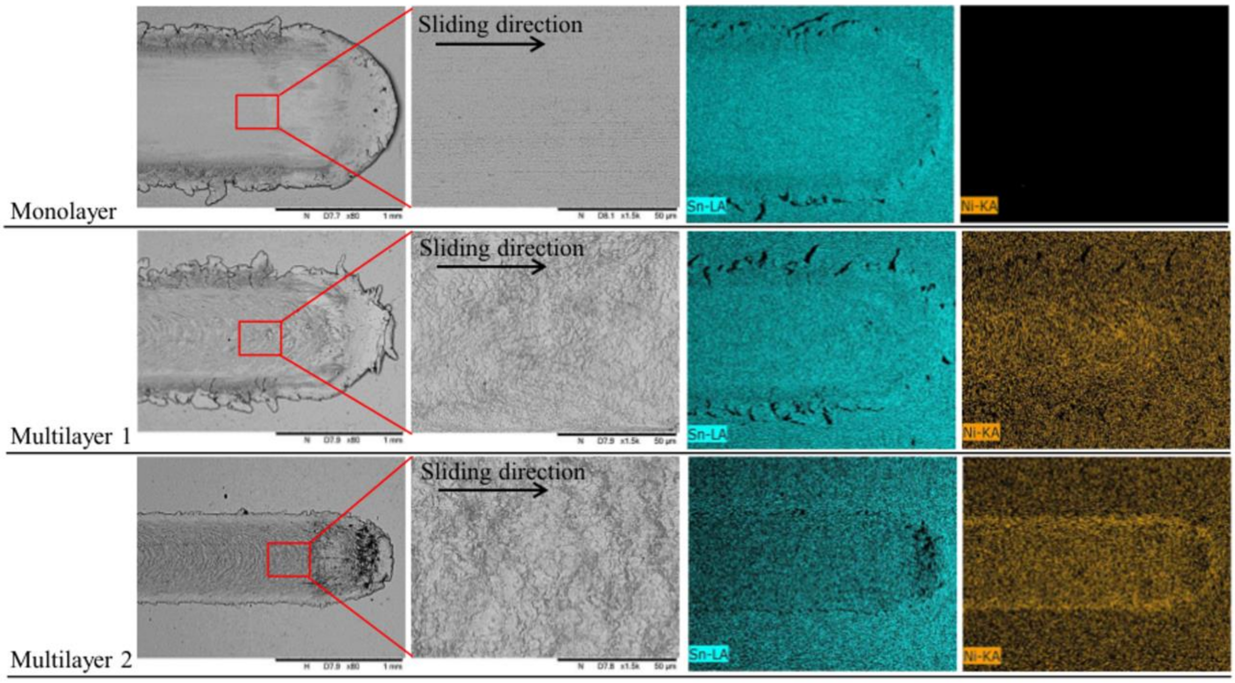

***Figure 7:** Scratch surface of Sn based coatings; SEM micrographs (at magn. 80x and 1500x) and EDX elemental maps (at magn. 80x) of Sn and Ni after 50 scratches at 10 N.*

EDX mapping of Monolayer scratch (at 80x) from the surface (Figure 7) showed no evidence of Ni which is obvious since in this case Ni is only located in the anti-diffusion layer around 6 µm from the scratched surface. However, some indication of Ni was observed in Multilayer 1 as the top Sn-Cu sublayer was slightly remaining and Si-Ni intermetallic phases were exposed at some localised points within the scratch. Higher signals of Ni in the case of Multilayer 2 evident much clearer exposure of Sn-Ni intermetallic phases. Figure 8 shows the cross-sectional microstructure and elemental maps of the three coatings after the multiple scratch test (50 scratches) at 10 N load. The presence of Sn-Ni intermetallic phases in the multilayered structures is clearly visible and supports the earlier observations taken from the surface.

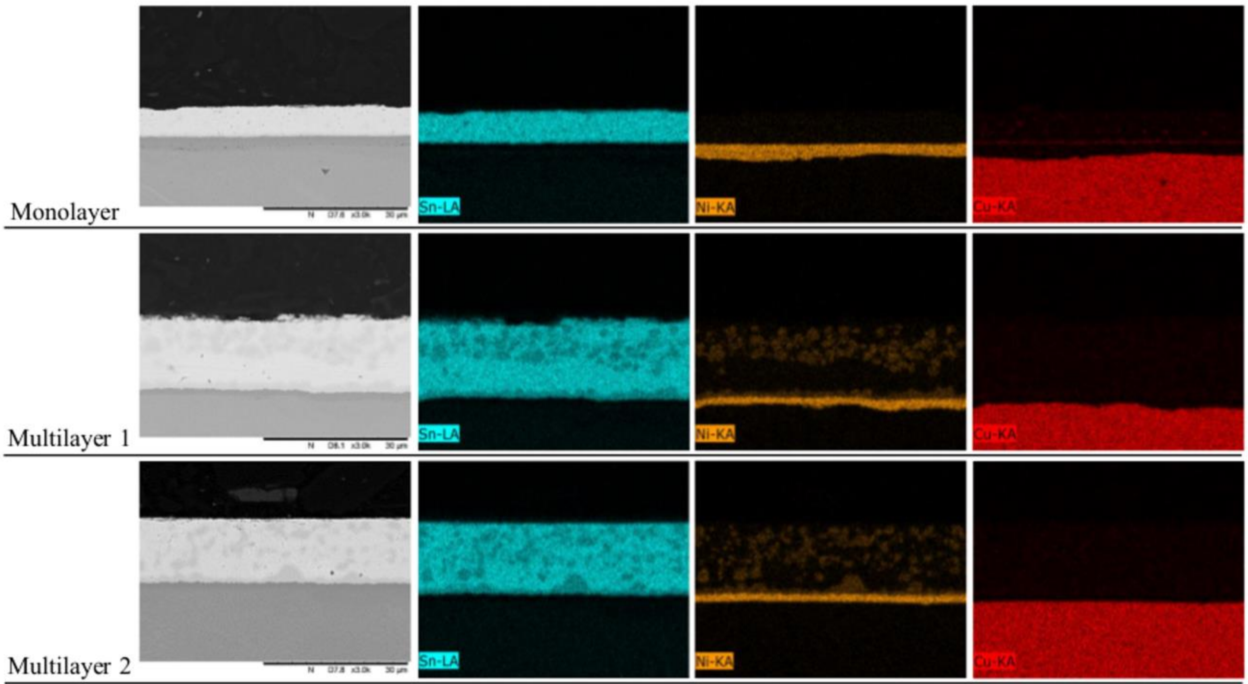

Figure 8: *Cross-section of Sn based coatings; SEM micrographs and EDX elemental maps of Sn, Ni and Cu at 3000x magn. after 50 scratches at 10 N.*

4. CONCLUSIONS

A novel multiple scratch test method was developed for characterising the tribological performance of three different soft tin based coating structures. The new method successfully captured the lubricious effects of SnNi intermetallic sublayer which helps reducing the friction at a greater extent. The improvement in wear resistance was achieved owing to increased hardness of coating structure due to the presence of hard SnNi intermetallic sublayer. It was also observed in case of Multilayer 2 (5-layers Sn based coating) that increasing the number of sublayers and bringing the intermetallic sublayer closure to the surface helps further reducing the wear.

ACKNOWLEDGEMENTS

The authors would like to acknowledge the European Commission for its funding through the European Union's Horizon 2020 research and innovation programme under grant agreement No 691503.

REFERENCES

1. Y. Zhang, I. Tudela, M. Pal, I. Kerr, High Strength Tin-based Overlay for Medium and High Speed Diesel Engine Bearing Tribological Applications. Tribology International, Vol. 93, Part B, pp. 687–695, 2016.
2. Y. Zhang, M. Pal, E. Banchelli, I. Kerr, Lead-free tin based multilayer overlay for Plain Bearing, UK patent application No: 1411055.5, 2014.
3. Y. Zhang, M. Pal, E. Banchelli, I. Kerr, Structure and Fabrication Method of Multilayer Overlay for Plain Bearings of Internal Combustion Engine, UK patent application No: 1411054.8, 2014.
4. M. Anand, Y. Zhang, I. Tudela, I. Kerr, V. Song, M. Pal, Evaluation of tribological performance of novel multilayer tin-based overlays for plain bearing applications. In: Ecotrib 2015 European Conference on Tribology 2015, 3-5 June 2015 Lugano, Switzerland.
5. K. Holmberg, A. Matthews, H. Ronkainen, Coatings tribology—contact mechanisms and surface design. Tribology International Vol. 31, Nos 1–3, pp. 107–120, 1998.
6. V. Jardret, H. Zahouani, J.L. Loubet, T.G. Mathia, Understanding and quantification of elastic and plastic deformation during a scratch test, Wear, 218:8–14, 1998.
7. A.J. Perry, The adhesion of chemically vapour deposited hard coatings to steel—the scratch test, Thin Solid Films, 78:77–93, 1981.
8. P.A. Steinmann, H.E. Hintermann, Adhesion of TiC and TiCN coatings on steel, J Vac Sci Technol A3:2394–400, 1985.
9. J. Valli, A review of adhesion test methods for thin hard coatings, J Vac Sci Technol, A4:3001–14, 1986.
10. H.E. Hintermann, Adhesion, friction and wear of thin hard coatings, Wear, 100:381–97, 1984.
11. A.J. Perry, Scratch adhesion testing of hard coatings, Thin Solid Films, 107:167–80, 1983.
12. P.J. Blau, Friction Science and Technology: From Concepts to Applications, CRC press, 2012.
13. M. Anand, M. Hadfield, J.L. Viesca, B. Thomas, A. Battez Hernández, S. Austen, Ionic liquids as tribological performance improving additive for in-service and used fully-formulated diesel engine lubricants. Wear, 334-335, 67-74, 2015.
14. J.L. Viesca, A.H. Battez, R. González, T. Reddyhoff, A.T. Pérez, H.A. Spikes, Assessing boundary film formation of lubricant additivised with 1-hexyl-3- methyl imidazolium tetrafluoroborate using ECR as qualitative indicator, Wear, 269, 112–117, 2010.

15. M.Ö. Bora, O. Coban, T. Sinmazcelik, V. Günay, M. Zeren, Instrumented indentation and scratch testing evaluation of tribological properties of tin-based bearing materials, Materials and Design, 31, 2707–2715, 2010.
16. K. Kato, K. Adachi, Wear Mechanisms, in: B. Bhushan, Modern Tribology handbook, CRC Press, Boca Raton-London-New York-Washington D.C., 2000.
17. I.J.T. Montes, Novel ultrasound-assisted electrodeposited Ni-based coatings for bearing applications, in: PhD thesis, 2015.
18. W. Wang, R.N. Singh, Influence of the microstructure on the mechanical properties of Ni/Sn multi-layered composites, Mater Sci Eng, A271:3064, 1999.