EVALUATION OF THE WEAR RESISTANCE BEHAVIOR OF ZN-NI AND ZN-NI/SIO$_2$ COMPOSITE COATINGS

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Abstract

The sliding wear resistance behavior of Zn-Ni and Zn-Ni/SiO$_2$ composite coatings were investigated using a sliding wear rig. Wear behavior was mainly evaluated based on weight loss measurements. Effect of applied load and no. of cycles on the weight loss of the coatings were given particular attention. Field Emission Gun Scanning Electron Microscopy (FEGSEM) was used to investigate the wear tracks to determine the prevalent wear mechanisms. It was found that weight loss of Zn-11%Ni/1%SiO$_2$ was lower than those of Zn-11%Ni and Zn-11%Ni/11%SiO$_2$ with a constant load of 10N and increasing number of cycles. Their weight loss took the following trend; Zn-11%Ni/1%SiO$_2$<Zn-11%Ni<Zn-11%Ni/11%SiO$_2$. However, with increasing normal load, all three systems of coatings exhibited a mixed response at a constant cycle of 100. At a higher load, a reverse trend to that of a lower load was observed. At 10N the weight loss of Zn-11%Ni<Zn-11%Ni1%SiO$_2$<Zn-11%Ni/11%SiO$_2$ while at 25N it took a reverse trend where weight loss of Zn-11%Ni/11%SiO$_2$<Zn-11%l%SiO$_2$<Zn-11%Ni. Morphology of the wear tracks revealed that the wear mechanism of Zn-Ni/SiO$_2$ coatings were mainly a function of particle content. Optimum wear resistance behavior was observed for coatings of Zn-Ni containing 1wt% SiO$_2$

Keywords: Zn-Ni electrodeposition, composites, wear resistance, SiO$_2$ nanoparticles

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1. INTRODUCTION

The effective use of zinc and its alloys as sacrificial coatings is widely reported [1-3]. Research on these coatings has evolved tremendously over the years from the traditional zinc coatings to its alloys and recently their composites. The systematic development of these coatings is due to the increasing demand for more durable coatings needed for use in more aggressive working conditions [4,5] such as wear which is a major factor responsible for the breakdown of most simple and complex machines. During contact of two surfaces in relative motion, wear is the damage of a solid surface involving progressive loss of materials. Wear between two unlubricated surfaces in relative motion one against the other presents several interactions both on the macroscale and nanoscale [4]. Zinc and its alloys are relatively soft and ductile; and are highly prone to wear and degradation when in contact with, and in sliding motion relative to another surface. For instance high strength steel fasteners used in automotive and aerospace industries are often coated with Zn- or Cd-based coatings for anodic protection [7]. In addition to corrosion protection, it is important for the coatings to have sufficient wear resistance to withstand the wear and abrasion during handling and torquing of the fasteners [2]. One way to improve the corrosion or wear resistance of these coating is to co-deposit the relevant second phase particles such as Al$_2$O$_3$ [8,9], SiO$_2$ [4,10,11], or solid lubricants such as transition-metal (TM) dichalcogenides (MoS$_2$,WS$_2$, NbS$_2$, etc.) [12] via composite electrodeposition. In this study, the wear resistance behaviour of Zn-Ni and Zn-Ni/SiO$_2$ composite coatings were investigated and its findings reported.

2. MATERIALS AND METHODS

2.1 Production of Coatings

The composite coatings were produced from acid sulphate Zn-Ni/SiO$_2$ baths containing ZnSO$_4$. 7H$_2$O 57.5 g/l, NiSO$_4$. 6H$_2$O 131 g/l, Na$_2$SO$_4$.10H$_2$O 162 g/l, SiO$_2$ 13-52 g/l. Silica particles of approximately 20 nm in aqueous suspension were used (both from Alfa Aesar). Agitation was effected using vibro-agitation with a vibromixer [13]. The diameter of the perforated plate attached to the vibromixer, which effected the agitation was 4.5 cm. A Zenith Variac supplied power to the vibromixer. Coatings were electroplated onto mild steel. Prior to electrodeposition, the mild steel panels were first cathodically cleaned in an alkaline bath containing 25.0 g/l of NaOH, 25.0 g/l of Na$_2$CO$_3$ and 50.0 g/l of Na$_3$PO$_4$ and etched in 50 vol.% (S.G 1.18) hydrochloric acid for approximately 20 seconds, washed in running tap water and then in deionised water. They were then transferred immediately into the bath for electroplating to avoid re-oxidation of the surface. All the electrodeposition experiments were carried out galvanostatically using DC currents. The anode material in all cases was 99% zinc foil. Coating compositions and morphologies were analysed using Field Emission Gun Scanning Electron microscope (FEGSEM) fitted with an energy dispersive analysis (EDX) facility. Weight percent of silicon in the deposits was analysed with the EDX analyser and converted to the weight percentage of silica.

2.2 Wear Studies

The test method utilised was based on a linear reciprocating ball-on-flat plane geometry described in ASTM Standards, designation; G 133-95. The direction of the relative motion between the sliding surfaces reverses in a periodic fashion such that sliding occurs back and forth and in a straight line. The wear rig used in the investigations was custom made. The entire wear procedure involved the reciprocatory motion of a compartment of lubricating bath (without lubricants) with the test sample rigidly fitted to its base against a stationary steel ball bearing with a normal load applied to it. Normal loads of 10N and 25N were used. The relative humidity was 40% and the lengths of stroke approximately 2.5 cm. Each friction pair (ball and flat specimen) was ultrasonically cleaned in acetone before and after each test to remove any possible surface contaminants and wear debris. The spherical steel ball bearing already clamped to its holder was lowered onto the flat specimen ensuring that the reciprocating drive shaft motion was horizontal and parallel to the surface of the flat specimen. The desired load was then applied and the wear process initiated. The degree of wear resistance was deduced based on weight loss using electrical balance with 0.01mg accuracy. Three replicate tests were carried out for each specimen condition, so as to minimize data scattering, and their average reported in this work. Morphologies of the wear tracks were studied using a Field emission gun scanning electron microscope (FEGSEM).
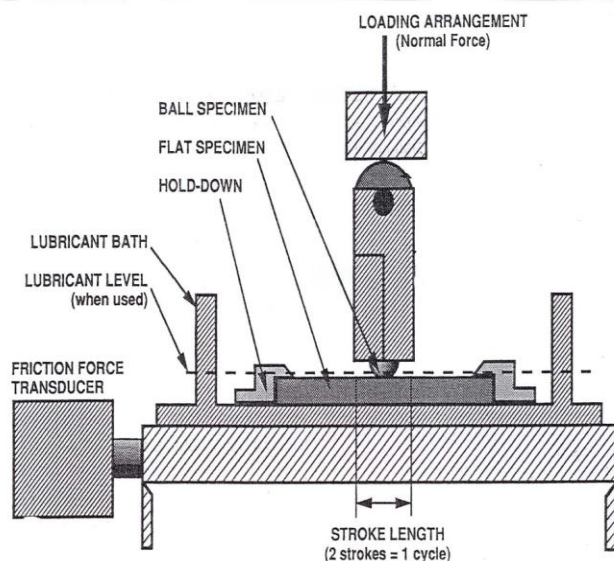

Fig. 1 Schematic diagram of the reciprocating wear test (Adapted from [14] with slight modifications)

3. RESULTS AND DISCUSSION

3.1 Effect of Increasing Cycles

Fig 2 shows the wear resistance behavior in terms of weight loss versus number of wear cycles on Zn-Ni and Zn-Ni/SiO$_2$ coatings containing 1 wt % and 11 wt % of 20 nm SiO$_2$ particles respectively. Weight loss of the coatings without SiO$_2$ and those with 11 wt% SiO$_2$ appears to take an increasing trend whilst coatings with only 1wt% SiO$_2$ shows

a mixed response with increase in the number of cycles. However, a unique trend in this figure is the magnitude of weight loss for each of the coatings. For all the number of wear cycles investigated, the weight loss values for the coating with 1 wt % SiO$_2$ were lower than those of the Zn-Ni alloy and the alloy with 11 wt% SiO$_2$ while weight loss values for the Zn-Ni alloy were lower than coatings with 11 wt% SiO$_2$. This implies that the wear resistance of Zn-Ni alloy is improved in the presence of approximately 1 wt% SiO$_2$ but reduced at 11 wt% SiO$_2$. Friction coefficient and wear rate of alloys decreases with increasing silicon content up to 2 wt% Si, but increases as the silicon content increases above this level due to particles coarsening and gathering in certain places leading to silicon free area and thus reduction of its reinforcement effect [15]. Cracking behavior of such alloys was attributed to the uneven distribution of silicon particles in the alloy [15]. This behavior can be related to that of agglomeration in composite electrodeposition which often appears to be detrimental to the integrity of the coatings. Also, the addition of 1% silicon into zinc-based alloys increases their tensile strength, hardness and wear resistance but reduces ductility [16].
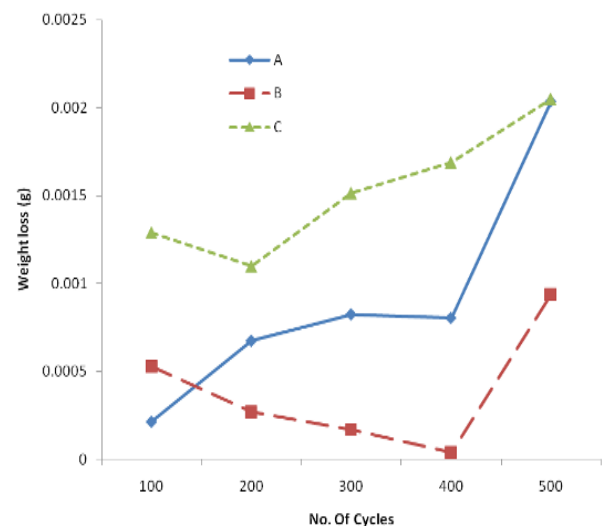

Fig. 2 Wear behaviour of Zn-Ni/SiO$_2$ electrodeposits containing 11%Ni and different amounts of 20 nm SiO$_2$ particles. (A) 0% SiO$_2$ (B) 1% SiO$_2$ (C) 11% SiO$_2$. Load 10 N

The results presented in Fig 2 are in agreement with the other investigators [17]. For both powder processed methods and electrodeposited methods, coatings with the highest amount of particles exhibited the highest erosion rates [17]. Similarly, Fig 3(a-c) shows the surface morphology of Zn-11%Ni, Zn-11%Ni-1%SiO$_2$ and Zn-11%Ni-11%SiO$_2$ coatings respectively. The presence of cracks is quite evident in the coatings containing the highest amount of SiO$_2$ particles (see Fig 3c). Generally, cracks are points of weakness in coatings and could lead to brittle fragmentation caused by increased microcracking tendency due to the reinforcement phase [18]. It is therefore not surprising that a coating with such cracks showed the weakest resistance to wear
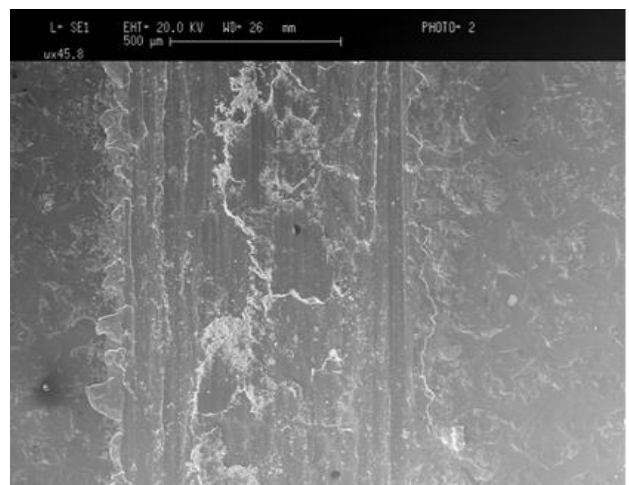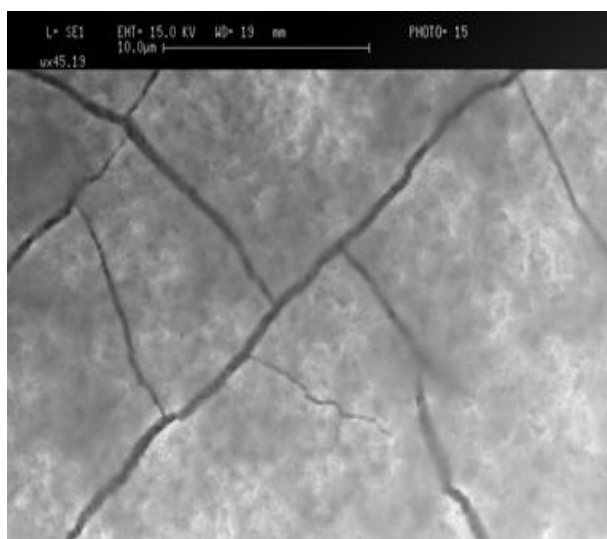
(a)
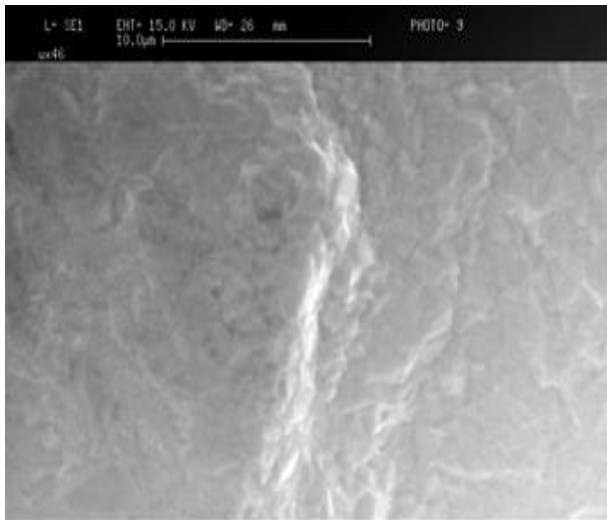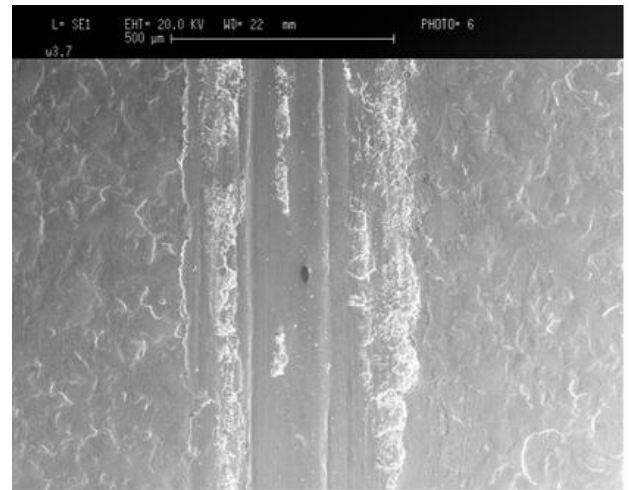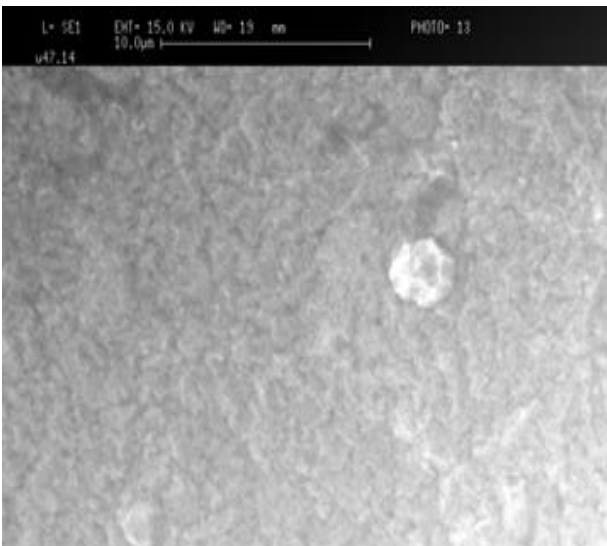
(b)

(c)

Fig 3. SEM micrographs showing morphologies of (A) Zn-11%Ni (B) Zn-11%Ni 1%SiO$_2$ (C) Zn-11%Ni-11%SiO$_2$.[5]

(a)

(b)

Fig. 4. SEM micrographs of wear surfaces of (a) Zn-11%Ni and (b) Zn-11%Ni/11%SiO$_2$ Load 20 N and 100 cycles. [5]

Fig 4 shows the surface morphologies of typical worn grooves of (a) Zn-11% Ni and (b) Zn-11% Ni-11%SiO$_2$. It is evident from this figure that the severity of the damage and the size of the worn surface of the coating with 11% SiO$_2$ were greater than that without particles. This appears to corroborate results in Fig 2 and suggest that the wear resistance of Zn-11%Ni-11%SiO$_2$ is much lower than the same alloy without particles in the coating. Also, the morphologies of the worn surfaces show the presence of material waves [19,20] for the coatings with 11% SiO$_2$, while such features were less obvious for the coatings without particles. Material waves tend to occur when coatings with cracks are subjected to wear (see Fig. 3c).

Reasons for the improvement in wear behavior of the coatings with 1 wt%SiO$_2$ and reduction with 11 wt% SiO$_2$ as shown in Fig 2 are not very clear. However, a possible explanation is that with lower particle contents of these coatings which were produced from baths with relatively lower bath particle loading of 26g/l SiO$_2$, the dispersion of the particles in the alloy matrix may have been relatively homogeneous since lower levels of agglomeration were

expected, but at excessively high contents of particles in the bath, agglomeration occurs leading to the incorporation of agglomerates in the deposit. Incorporation of such pockets of agglomerates could lead to localised stress, which possibly contributed to the crack propagations obvious in Fig 3 (c) and hence the high rate of wear observed in Fig 4 for coatings containing 11% SiO$_2$, possibly due to 'ploughing' effect of agglomerated particles.
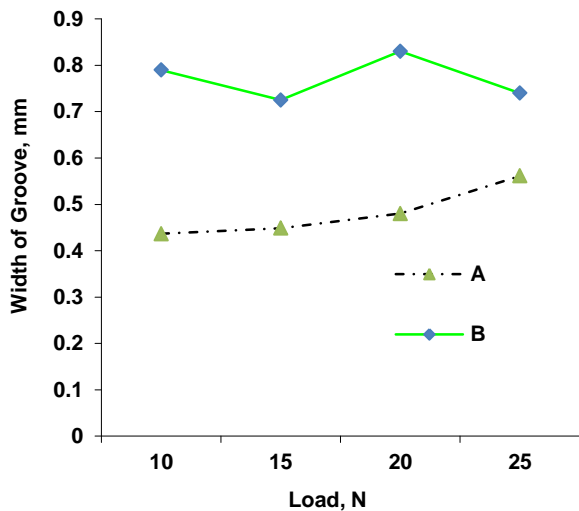

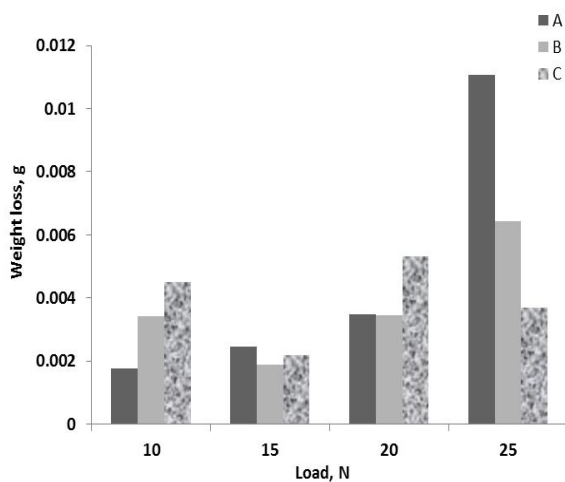**Fig. 5** Width of worn groove versus applied load for (A) Zn-11 %Ni and (B) Zn-11%Ni-11%SiO$_2$ coatings

Fig. 6 Weight loss versus increasing load for (A) Zn-11%Ni (B) Zn-11%Ni-1%SiO$_2$ (C) Zn-11%Ni-11%SiO$_2$. 100 cycles

As further evidence of the poorer wear resistance behavior of coatings with the highest amount of SiO$_2$ particles, Fig 5 shows the width of each worn groove as a function of increasing load for Zn-11%Ni and Zn-11%Ni-11%SiO$_2$. For all the loads applied, width of the wear track for the coatings with 11%SiO$_2$ was much larger than those without particles in the coating. This is an indication that coatings with 11%SiO$_2$ were less resistant to wear than those without particles for the prevalent experimental conditions.

3.2 Effect of Increasing Load

Fig 6 shows the influence of increasing load on the wear behavior of Zn-11%Ni, Zn-11%Ni-1%SiO$_2$ and Zn-11%Ni-11%SiO$_2$ at 100 cycles. For the range of loads investigated, the weight loss tends to show a mixed response with increasing normal load. At a lower load of 10 N, the weight loss is lower for the coating without particles and increases with increase in amount of particles in the coatings. At slightly higher loads of 15 and 20 N, weight loss of all three types of coatings tends to normalize. However, at the highest load of 25 N, reverse is the case where the weight loss becomes higher for the coatings without particles and decreases with increasing amount of particles. Zinc-based matrix alloy exhibited lower wear rate than that of the composite prior to seizure and the trend reversed during seizure [21]. This behavior has been attributed [21] to the difference in lubricity, thermal stability and load bearing characteristics of microconstituents of the individual coatings. The low melting characteristics of various microconstituents in the (zinc-based) matrix alloy enables it to perform better than the composite at low operating temperatures (generated at low speed/pressure) only. On the contrary, higher thermal stability imparted by the particles could cause the composite to exhibit better wear properties at higher operating temperatures generated at high speed/pressure [21]. This was probably the case with the present work as evident in Fig 6 where the weight loss for the coating without SiO$_2$ particle was lower than those of the composites with SiO$_2$ and increased with increasing amount of particles in the coatings at a load of 10 N. On the contrary, the weight loss was highest for the coating without particles and decreases with increase in particle content of the coating at 25 N. A possible reason for this behavior is that at a lower load of 10 N, the major microconstituent (i.e zinc-rich phase η) of the zinc-alloy matrix, with a lubricating nature [22] probably acted as a solid lubricant, leading to lower coefficients of friction, and hence better wear resistance. However, the microconstituent of the (zinc-based) alloy system being a low melting material is restricted in its positive role to lower operating temperatures [23-24]. Generally frictional heating is likely to be higher at more severe conditions (i.e higher loads). Increasing frictional heating causes larger adhesion of the sample material to the disc making the occurrence of wear more probable [25]. The presence of particles could reduce such frictional heating in case of the composite than the alloy by reducing the effective area fraction of the matrix part of the sample in contact with the counterface [21]. Accordingly, (excessive) adhering tendency of the composite with the counterface reduces over the matrix alloy under identical test conditions, thereby decreasing the extent of frictional heating [21]. This behavior probably accounted for the observed higher wear rate of the alloy without SiO$_2$ particles at a higher load of 25 N as compared to its composite counterparts in Fig 6. It is evident that at 25 N the weight loss decreases with increase in SiO$_2$ content of the coatings. Although Fig 6 generally tends to exhibit a mixed response to increasing load, there is a general tendency for the weight loss of Zn-11%Ni and Zn-11%Ni-1%SiO$_2$ to increase with increasing Load while that of Zn-11%Ni-11%SiO$_2$ shows an inconsistent trend.

4. CONCLUSIONS

- Wear resistance behaviour of Zn-Ni and Zn-Ni/SiO$_2$ coatings with different amounts of SiO$_2$ particles shows that weight loss of Zn-11%Ni/1%SiO$_2$ was lower than those of both Zn-11%Ni and Zn-11%Ni/11% SiO$_2$. The wear resistance of these coatings all with 11%Ni took the following order; coatings with 1 wt %SiO$_2$> 0 wt %SiO$_2$> 11 wt %SiO$_2$ with increasing number of cycles.

- With increasing normal load, the coatings tend to exhibit a mixed response at a constant cycle of 100. At a higher load, a reversed trend to a lower load was observed. The difference appears to be due to differences in lubricity as a function of thermal stability of the individual coatings as a result of frictional heating. Also, possible compaction of porous sites which may have occurred due to possible codeposition of agglomerates and strain hardening with the higher load appears to play key role in the differences in their wear behavior.

- Morphologies of the worn grooves were dissimilar with changes in SiO$_2$ content of the coatings. Worn grooves of Zn-11%Ni/11% SiO$_2$ exhibited re-current wave forms in contrast to that without particles and with 1% SiO$_2$, indicating the presence of a high density of cracks due to the large amount of particles incorporated.

- Although, 1wt%SiO$_2$ content appears to be the optimum value for best wear resistance in the set of coating systems studied, the range of difference in particle content between each of them is quite wide. For a better understanding, optimization of coatings with a closer range of particle content and determination of their coefficient of friction may be necessary.

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