Comparative Study on Dry Sliding Wear Behaviour of TiAlN, ZrAlN and ZrN/Al_2O_3 Hard Coatings on ZA Alloys

B. Harish, K. R. Prakash, and R. Suresh

Abstract The objective of the paper mainly discusses on effects of coating each one of the below materials namely TiAlN, ZrAlN and $ZrN + Al_2O_3$ on ZA-27 alloy specimens to understand wear resistance characteristics of such coated composite by cathodic arc coating techniques, also investigation was made on their composition, structure, hardness and wear behaviour at constant coating thickness using profilometer, EDX, SEM and pin on disc, respectively, at room temperature. The hardness of the $ZrN + Al_2O_3$, TiAlN and ZrAlN are 29.06 GPa, 24.49 GPa and 22.06 GPa, respectively, and the microstructure reveals that $ZrN + Al_2O_3$ exhibited outstanding properties compared to other two because of columnar structure, dense grain size and multilayer coatings. Also, $ZrN + Al_2O_3$ exhibited superior wear resistance than TiAlN and ZrAlN due to the Al_2O_3 layer present on the upper layer of ZrN which prevents the effect of oxidation and reduces friction between tool and work piece.

Keywords Hard coatings · Cathodic arc coating technique · Microstructure · Wear · TEM

1 Introduction

The zinc-aluminium alloys (ZA27) are potential alloy to replace brass and steel for wear resistance machinery components especially used as bearing material due to lower friction coefficient [1], good wear resistance and good damping properties. The

B. Harish (✉)
Department of Mechanical Engineering, Maharaja Institute of Technology, Mysore, Karnataka, India

K. R. Prakash
Department of Mechanical Engineering, The National Institute of Engineering, Mysore, Karnataka, India
e-mail: krp@nie.ac.in

R. Suresh
Department of Mechanical Engineering, VTU Center for PG Studies, Mysore, Karnataka, India

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performance and life of the ZA bearings depends upon the surface properties and coefficient of friction between materials. However, ZA alloy material does not meet with the industrial requirements such as high speed and high load, hence they are restricted in automobile applications. Because of its good wear resistance properties of ZA-27 alloy many researchers put their effort to enhance the wear resistance of this alloy by heat treatment, addition of alloying elements, hard particle reinforcement and protective coatings [2–5]. The results have showed that the coated specimens are performing at high temperature approximately 600 °C which is generated during the wear process at high speeds and loads. Hence, the coated specimens are thermally stable at high temperature [6] and suitable as bearing materials. Nitride-based hard coatings are widely used as coating material for bearing because of outstanding hardness and wear resistance. They also provide corrosion protection in the form of a passivation layer on the components [7]. Addition of Al element into nitride material further improves wear resistance at higher temperature and these results were recorder by many researchers. However, ZrAlN coating on ZA-27 is very less explored which is the partial miscibility gap between ZrN and AlN, which makes a heterogamous mixture than that of homogeneous materials. ZrAlN and ZrN/Al_2O_3 are possible alternative candidates for well-established TiAlN and CrAlN hard coatings. But ZrAlN stability always depends on deposition technique and aluminium content of 0.3–0.5 based on density functional theory [8–10] so far all metal nitrade and carbo-nitrade coating on the surface of ferrous materials using physical vapour deposition techniques were done reported [11]. Also as per author knowledge no researchers worked on metal nitrade coated on nonferrous metal like aluminium, ZA, copper, etc. there is an apparent lack of information regarding the wear resistance of nitrade coating. The objective of the work is to investigate on chemical composition, morphological, micro hardness and wear properties of TiAlN, ZrAlN and ZrN/Al_2O_3 hard coatings on ZA alloys by cathodic arc evaporation has been chosen for synthesis to present result intended to determine the best potential candidate for bearing applications.

2 Experimental Study

2.1 ZA Specimen Preparation

The present work ZA-27 alloy was selected as a base material, and its chemical composition as per ASTM standards (Al-25%, Cu-2%, Mg-0.01, Zn-balance). The specimens (12 mm diameter and 35 mm length) were prepared using liquid metallurgical technique. Wear cylindrical specimens (pin) of 8 and 20 mm were machined from the prepared casting. Then, both the circular face of the cylindrical surface was polished for a smooth surface as per standards before coating.

2.2 Coating on ZA Circular Surfaces

Vaporised material impinges on the substrates and forms a thin layer of coating. The two target materials for TiAlN are Ti and Al blocks. Similarly for ZrAlN, Zr and Al blocks are used in the process and allow nitrogen and oxygen gas alternatively one after the other. Also Ar/N_2 gas is used to ensure high degree of ionisation, the pressure that is maintained during the process in the chamber is about 1–1.5 Pa. This process provides uniform distribution of the coatings on the substrate.

2.3 Surface Roughness Characterisation

After coating of the specimens, the roughness of the samples is held in the wax mould to avoid any disturbance during the movement of stylus then they are characterised using MAP3D-25 stylus profilometer to determine the surface roughness of the deposited coatings. The six samples were selected for each condition and measured the average roughness of coatings deposited.

2.4 Surface Morphology Studies

The coated specimens prior to conduct surface morphology are cleaned with acetone to remove any impurities/dust particle. For each run samples were mounted in the scanning electron microscope for the analysis, the samples are mounted in the chamber on a small carousel with small pellets using clay glue to investigate the coatings structure and grain boundaries. The coated specimen chemical compositions were determined by using Qunato FIG 600 energy dispersive spectroscope analyser.

2.5 Hardness Test

Hardness of the polished coated specimens was measured using Matsuzawa Hardness Tester MMT–X7A on Vickers hardness. The diamond pyramid type indenter was used for a load of 10 g with dwell time of 20 s. The hardness values were computed as per standard formula.

2.6 Wear Test

The wear test was conducted as per ASTM G99 standard at dry condition using pin on EN 24 material disc test rig diameter of 200 mm and surface roughness was 2 μm and its hardness of BHN 229. Before wear test both counter disc and wear specimen were cleaned by washing with acetone to remove traces of grease. The weight loss was measured using electronic balance of nearest 0.1 mg. The wear tracks were made on the pin on disc machine with normal loads of 20, 40, 60, 80 and 10 N and which was run for a total of 1000 cycles at 100 rpm in dry condition. This was done to ensure that enough particles are being generated without high rise in temperature which might alter the properties of the pin.

3 Result and Discussion

3.1 Microstructure

Figure 1a–c shows transfer section for TiAlN, ZrAlN and ZrN + Al_2O_3 coated specimens on the ZA-27 alloy, respectively. The image shows the two different layers and their unevenness on the surfaces. The larger surface is ZA-27 alloy (host) and smaller layer respective coatings. All three type coating showed a columnar structure of oriented in (111) plane. At the interface between the matrix and coating material more porosity were observed in the case of TiAlN coated specimen as shown in Fig. 1a. Figure 1b shows transfer section image of ZrAlN coated specimen, which has columnar grain structure, which is similar to TiAlN with grain structure orientation of (111) direction. But some reduction in columnar structure was observed along with micro-particles on the coating surface, which promotes the roughness of the coatings. Figure 1c shows ZrN/Al_2O_3 multi-layered coated surface images, which has two clear distinction layers such as bottom ZrN and top Al_2O_3 layers. ZrN layer are identified by columnar structure in the direction of (111) and Al_2O_3 layer is much denser structure. The multi-layer coating has less cavities and porosity compared to ZrAlN and TiAlN coatings and few micro-particles are observed on the surface of the coatings. Due to combined effect of multi-layer expected more hardness values.

3.2 Surface Roughness of the Coatings

Stylus profilometer gives the surface roughness of the coated insert. The 3D image generated shows the type of surface morphology present on the coating. Figure 2a–c shows 3D representation of surface texture of TiAlN, ZrAlN and ZrN + Al_2O_3 coated specimens on the ZA-27 alloy, respectively. Figure 2a shows the average roughness is 0.003 μm. Low surface roughness indicates that the bearing will have

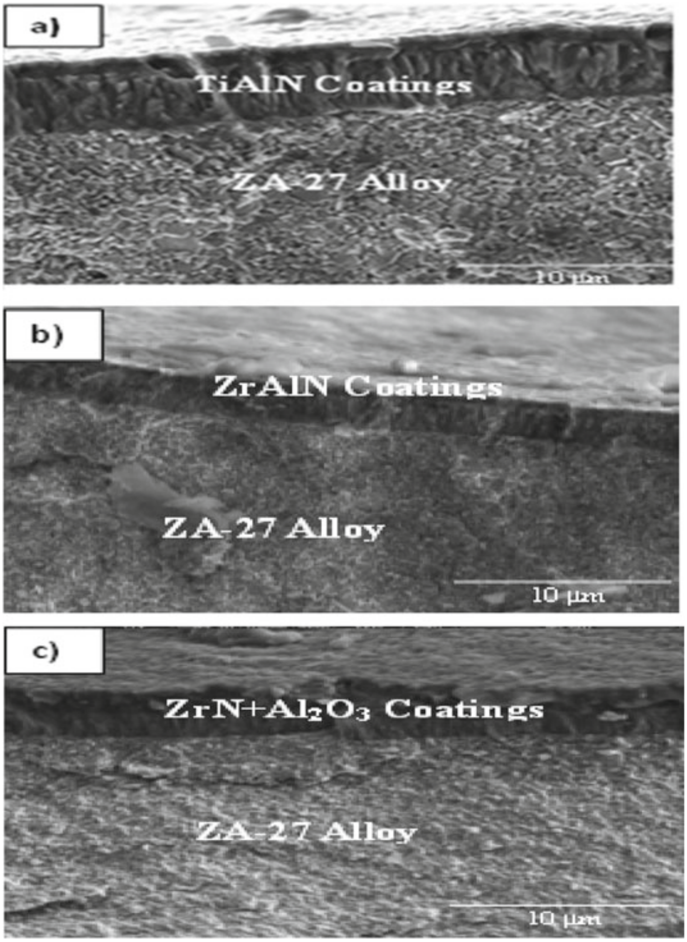

Fig. 1 SEM images of transfer section of coated specimens

better tribological properties and reduces the power consumption of the bearing. TiAlN and ZrN/Al_2O_3 show the least surface roughness, whilst ZrAlN shows slightly higher surface roughness. This could be due to micro-particles deposition due to impingement of sputtered particles during the coating process. In all the coatings, some porosity in the structure is observed which could be a reason for the roughness. The porous sites are the regions where the coating deposition is uneven.

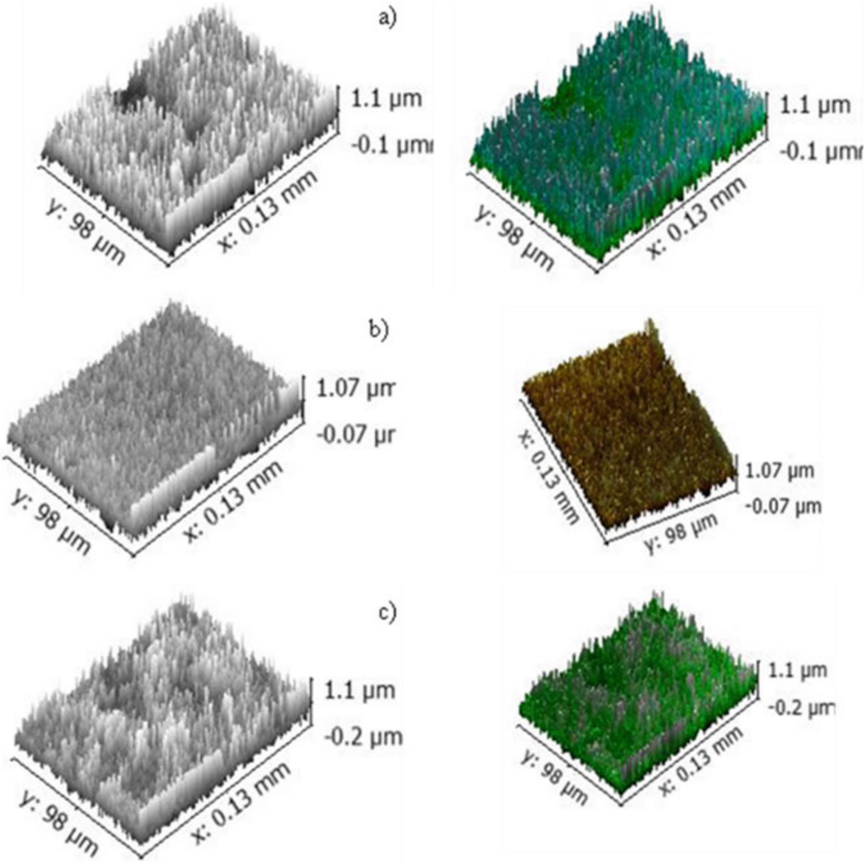

Fig. 2 3D images of ZA-27 coated with **a** TiAlN coating, **b** ZrAlN coating and **c** ZrN + Al2O3 coating

3.3 Energy Dispersive Spectrometry

Figure 3 (curve a) shows the EDS mapping of elements present in TiAlN coated specimen. It is found that the coating has 60.35% of Ti, 25.84% of Al and 13.81% of N. Excess Al content is not found in the coating. The EDS mapping (curve b) of elements present in ZrAlN coated specimen. The percentage composition in Zr is the highest in ZrAlN (53.71%) coatings, followed by Al (28.67%). The EDS mapping (curve c) of elements present in ZrN + Al_2O_3 coating. It is found Zr is the highest in proportion relative to all the elements. In all the three cases the percentage of oxygen is not detected as the atomic number, Z for oxygen is less than 11 and it is extremely difficult to detect any such element by EDS technique. Since all the coatings show very less proportion of nitrogen there could be a possible contamination by oxygen

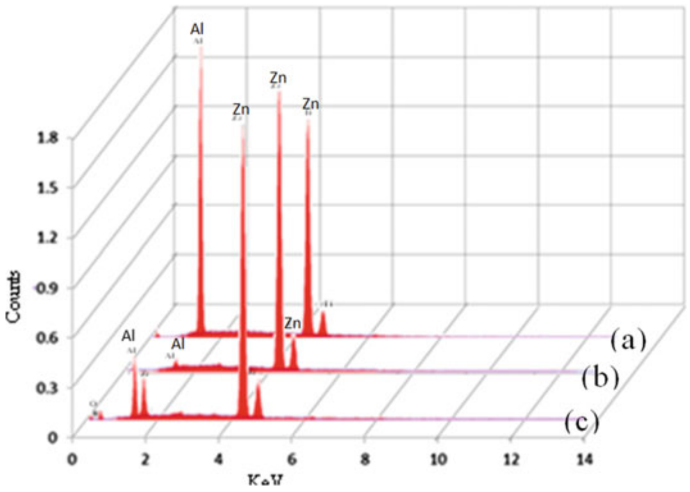

Fig. 3 Spectrum showing percentage of different elements present in **a** TiAlN coating, **b** ZrAlN coating and **c** ZrN + Al_2O_3 coating

(more than 3%) in all coatings. Similar findings are reported by Veprek and Veprek in Ref. [12].

3.4 Micro Hardness

Table 1 gives the results of Vickers microhardness test results performed on all the three coatings. It is observed that ZrN/Al_2O_3 coating showed the highest hardness among all the three types of coating. The increase in the hardness can be attributed to the Al_2O_3 layer which is known to improve the hardness of the ZrN coatings as suggested by many researchers [13, 14]. It has been found that Al_2O_3 layers have better hardness, high melting points. Hence, it can be concluded that Al_2O_3 acts as a beneficial layer in increasing the density and hardness of the coating. Further ZrAlN shows the second highest hardness compared to TiAlN, this is because Zr has larger lattice parameter compared to Ti and also the self-organising structure of ZrAlN into c-ZrN and w-AlN is known to improve its hardness.

Table 1 Hardness of the different coatings on ZA-27 alloy

Type of coating	Hadness (Hv 0.1)	Hardness (GPa)
TiAlN	2349	23.04
ZrAlN	2497	24.39
ZrN + Al_2O_3	2786	27.36

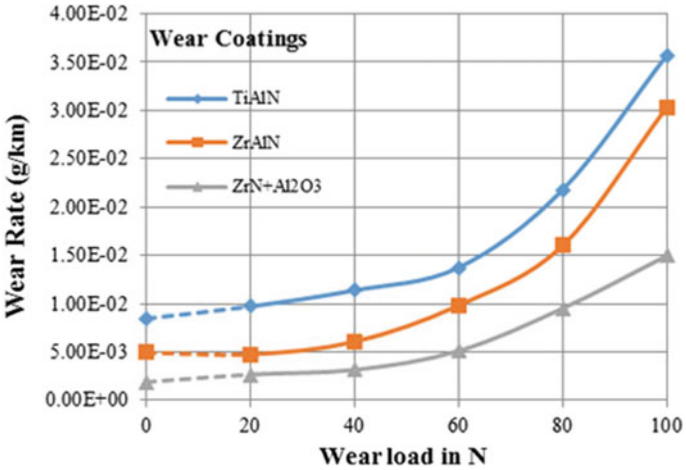

Fig. 4 The variation of wear rate plotted against wear load for three different coatings (dotted lines are extrapolated values)

3.5 *Wear Rates*

Figure 4 shows the variation of wear rates of the three coatings such as TiAlN, ZrAlN and ZrN + Al_2O_3 with wear loads of 20, 40, 60, 80 and 100 N. The wear rates are increasing with increasing wear loads in nonlinearly. The same trend was observed in all three coatings but the effect is more severe for TiAlN and ZrAlN coatings and less severe for ZrN + Al_2O_3 coating. The wear rate from 20 to 60 N almost linear in all three cases but wear transition occurs at 60 N then it is exponentially increased with loads. TiAlN and ZrAlN coatings were subjected to wear transition from mild wear to severe wear because of surface hardness, roughness and porosity in the coatings. Due to multi-layer coating of ZrN + Al_2O_3 increases hardness and reduces the porosity which leads to reduce the wear resistance.

3.6 *Coefficient of Friction*

Figure 5 shows a typical coefficient of friction results obtained on a pin on disc machine. This was done to obtain maximum frictional force thereby ensuring significant coating material transfer and particle generation.

From Fig. 5, it can be observed that the frictional force increases when the normal load increases irrespective of coatings. It is observed that the coefficient of friction is initially very high and then reduces steeply within 5–8 s, this is due to the change of static friction to dynamic friction and also wear track formation. It can also be observed that the coefficient of friction gradually reduces further down to a lower

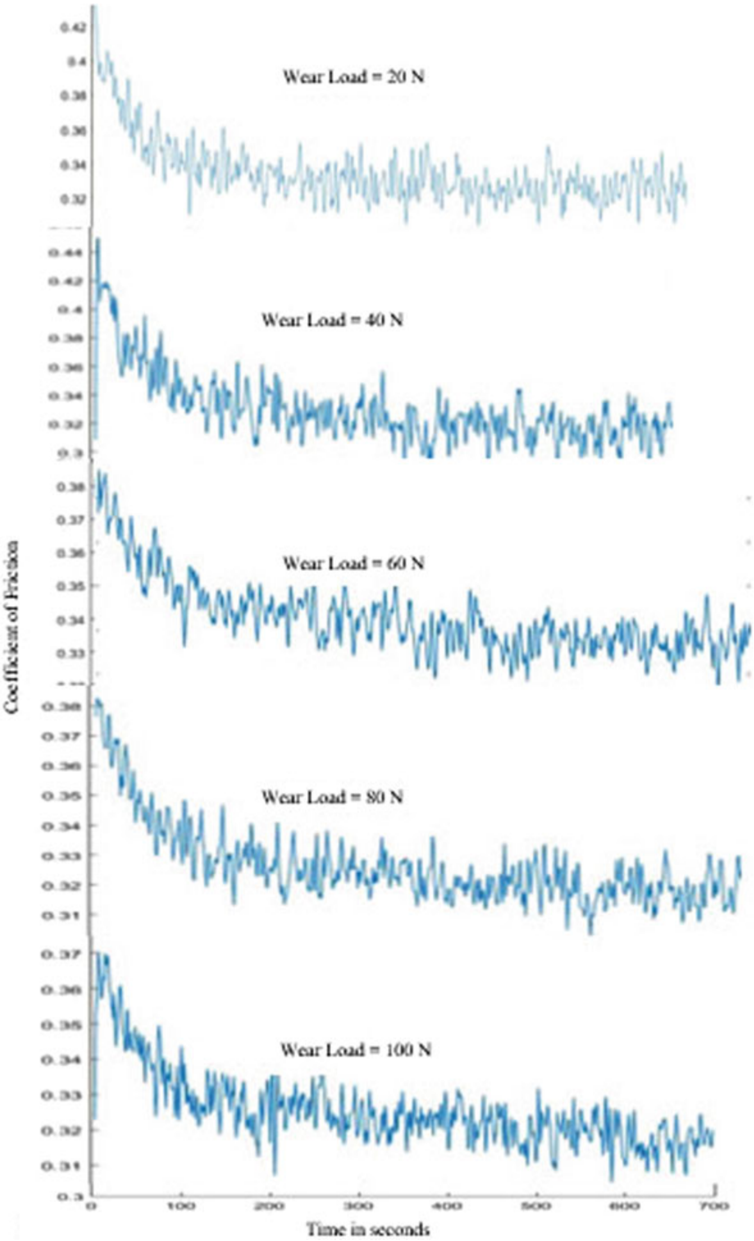

Fig. 5 A typical graph of coefficient of friction as a function for various loads of 20 N, 40 N, 60 N, 80 N and 100 N for TiAlN coated ZA-27 alloy

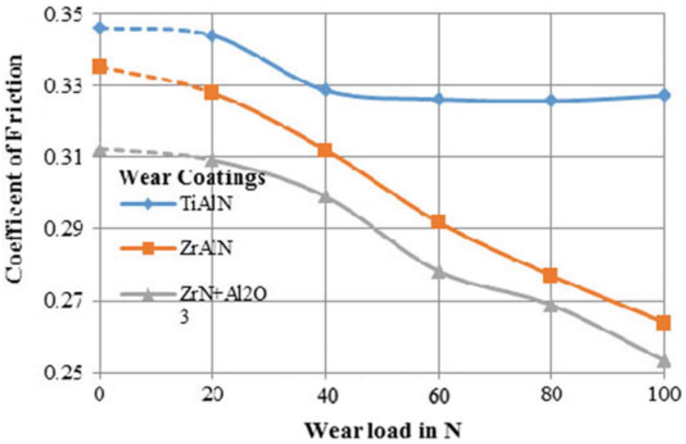

Fig. 6 Coefficient of friction as a function for various loads for TiAlN, ZrAlN and ZrN + Al_2O_3 coated ZA-27 alloy (dotted lines are extrapolated values)

level before obtaining a saturated value, this is due to the phenomena of adhesive wear. Initially, the friction is between the coating and the metal but later the coating degenerated from the pin gets adhered to the plate and gradually the friction between metal and coating becomes friction between coating to coating there by reducing.

As the coefficient of friction values determined are found to fluctuate about average values in all the cases for the selected ranges of sliding time of 700 s, the average coefficient of friction has been considered and its variation with wear load is shown in Fig. 6 for all three types of coatings. The coefficient of friction of all three type of coating decreases with increasing load but TiAlN coating specimens decreases up to 40 N then it maintained steady state coefficient of friction which may be metal to metal contact after the complete removal of coating on the surface.

4 Conclusion

1. ZrN/Al_2O_3 has the highest hardness of 27.32 GPa when compared to other two coatings. The dense grain structure and reduced grain size improves the coating hardness. Due to multilayer coating, the hardness improves.
2. EDS test shows the percentage of composition of the coatings. Percentage of Al is between 25 and 28% which helps in better hardness of the coating. Less percentage of nitrogen is present in all the coatings. The surface roughness of the coatings Ra, value between 0.02 and 0.03 μm.
3. SEM images show the columnar structure in TiAlN and ZrAlN. ZrN regions are identified by columnar grain in (111) direction and the Al_2O_3 layer is somewhat dense in its structure very less porosity and cavities are observed.

4. Wear rate of ZrN + Al_2O_3 coated specimen is significantly lower than the other two coating specimens
5. The average coefficient of friction of ZrN + Al_2O_3 multilayer coated samples is less than that of the other coatings and decrease with increasing wear load is observed.

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