

# Comparative Investigation of Effect of Diamond Like Carbon Coating and Ni<sub>3</sub>Al Coating on Tribological Properties of ZA-27 Alloy

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## Abstract

The objective of the research work was to investigate the effect of diamond like carbon coatings(DLC) and Ni<sub>3</sub>Al coating on microstructure, surface roughness, wear and friction of coated ZA-27 alloy prepared by plasma assisted chemical vapour deposition. The microstructure, chemical structure, surface roughness and wear were tested by scanning electron microscope, Raman spectroscopy, Surfcom Flex roughness tester and pin on disc test rigs respectively. The average coating thickness of DLC and Ni<sub>3</sub>Al are 2.16 mm and 2.74 mm respectively. The surface roughness was 0.411 and 0.434 mm for DLC and Ni<sub>3</sub>Al coatings respectively. The Raman spectroscopy showed that amorphous carbon with I<sub>D</sub>/I<sub>G</sub> ratio 0.85 for DLC but it is very low for Ni<sub>3</sub>Al coatings. The average wear rate of 15.369 and 22.45 mm and 0.275 and 0.432 coefficient friction were observed for DLC and Ni<sub>3</sub>Al coating respectively. The comparative studies showed that DLC coating on ZA-27 alloy showed superior wear resistance and lower coefficient of friction compared to Ni<sub>3</sub>Al coated specimens.

**Keywords:** DLC coatings, Ni<sub>3</sub>Al coatings, ZA-27 alloy, Chemical vapour deposition, Raman spectroscopy.

## 1. Introduction

Coating surfaces of the metal or non-metal have potential to strengthen the micro-textures and solid lubricants to enhance their wear resistance and reduce their friction coefficient properties [1-3]. Presently, most widely used hard wear resistant coatings are diamond like carbon(DLC) and Ni<sub>3</sub>Al coatings for wear and oxidation resistance applications[4&5]. DLC coatings have a unique mix of features such as high specific strength, chemically stable, low friction, biocompatibility etc. In infrared range DLC coatings have high transitivity hence they are used in surface protection for both wear and oxidation machine parts. DLC film is used for gas membrane barrier on polyethylene terephthalate bottles for beverages and food to protect scratch and UV rays [6]. Ni<sub>3</sub>Al superalloys find many applications in the modern aviation industry due to their good mechanical strength, wear resistance and oxidation resistance at higher temperature above 1000 °C [7]. On the other hand Ni<sub>3</sub>Al based coatings are used as protective coatings for gas turbine blades because of their high melting point, excellent corrosion resistance and high temperature oxidation.

DLC and Ni<sub>3</sub>Al coating was carried on different host materials in various techniques such as DC-plasma vapour deposition [9], high-power impulse magnetron sputtering, Plasma Enhanced Chemical Vapour Deposition [10], plasma-assisted chemical vapour deposition[11] and cathodic Arc deposition techniques [12]. For larger scale production of coating both physical deposition and chemical deposition methods were used. For control composition, morphological structure and tailored mechanical properties with lower defects, magnetron sputtering is used. The larger thickness and shorter time coatings, cathodic arc deposition technique was used for various coatings. Pulsed and high power impulse magnetron sputtering modes open additional possibilities for ceramic coatings that increase the tribological properties.

From the literature survey it has been found that a lot of work has been done on development of DLC Coating from plasma enhanced chemical vapour deposition (PECVD) process and Sputtering process. The substrate material used for various researches found to be titanium, and few alloy steels. Only few research work investigates and compares two different coatings for different properties. Present study focuses on deposition of DLC and Ni<sub>3</sub>Al coatings on ZA-27 alloy pin surface by hybrid plasma assist and chemical vapour depositions process. The objective of the work is to investigate on chemical composition, morphological, and wear properties of DLC and Ni<sub>3</sub>Al hard coatings on ZA alloys by cathodic arc evaporation techniques.

## 2. Experimental study

8 mm diameter and 20 mm length cylindrical specimens of ZA-27 alloy of composition of Al-25%, Cu-2%,Mg-0.01, Zn-balance were selected as a base materials for coating. Both the circular faces of the cylindrical surfaces were polished before

coating. Prior to the deposition of DLC on substrate, they are cleaned ultrasonically in acetone baths for 15 minutes and then dried in a chamber consisting of atmospheric nitrogen. The deposition was carried out in a hybrid system of CVD and PVD and the system was a combination of Magnetron sputtering and Plasma assisted Chemical Vapour Deposition (PACVD) process. The process magnetron sputtering was used to deposit a Ni<sub>3</sub>Al onto the substrate and PACVD was used to deposit DLC on the substrate. The system consists of two magnetron guns which can be biased by both DC and RF. The gun can be DC biased up to 1KW and RF biased up to 300W. The system is connected to a 13.56 Hz frequency generator. The substrate holder can also be DC and RF biased, they have both rotating and heating capabilities. Magnetron guns and substrate holders are cooled by water chiller. Various gauges are installed to measure the chamber pressure. The substrate is placed onto the fixtures for coating after it has been cleaned. The fixture is then placed in the coating chamber. By draining away the thin air in the chamber with a vacuum pump, vacuum is created inside the chamber. Preheating the substrate to a temperature of 200°C to 300°C is required. In the coating chamber, argon and ionised nitrogen are introduced. A vacuum arc flash evaporates and ionises chromium, resulting in plasma within the chamber. The process parameters of PACAVC are power 40 W, pressure of 125 mTor, duration of coating is 270 minutes, gas flow rate 75 cm<sup>3</sup>/s and CH<sub>4</sub>:Ar ratio is 83.17 for DLC, and Ni<sub>3</sub>Al sputtering target was used for Ni<sub>3</sub>Al coatings.

Both samples were polished as per standards and then etched for microstructure studies under scanning electron microscope. The Nikon Microscope LV150N with Clemex Image Analyzer was utilised to analyse microstructure in this study. The surface roughness of the both coated materials is measured using Zeiss Surfcom Flex 50A. Raman spectroscopy is used to characterise many types of carbon, including amorphous and crystalline carbon, and it is sensitive to the nature of carbon atom bonding. The disc material was EN31 steel with a diameter of 200mm and surface roughness was maintained to 2µm. The pin was held against the rotating disc with a wear track of 100mm. The pin was loaded against the disc through the dead weight loading system. The wear test of specimens were conducted under normal load of 10N, 20N, 30N and with a disc rotating speed of 100rpm, 200rpm and 300rpm with the sliding distance kept constant at 1000m. In the present experiment the parameters such as speed, time and load are varied throughout the experiment.

### 3. Result and Discussion

#### 3.1 Microstructure

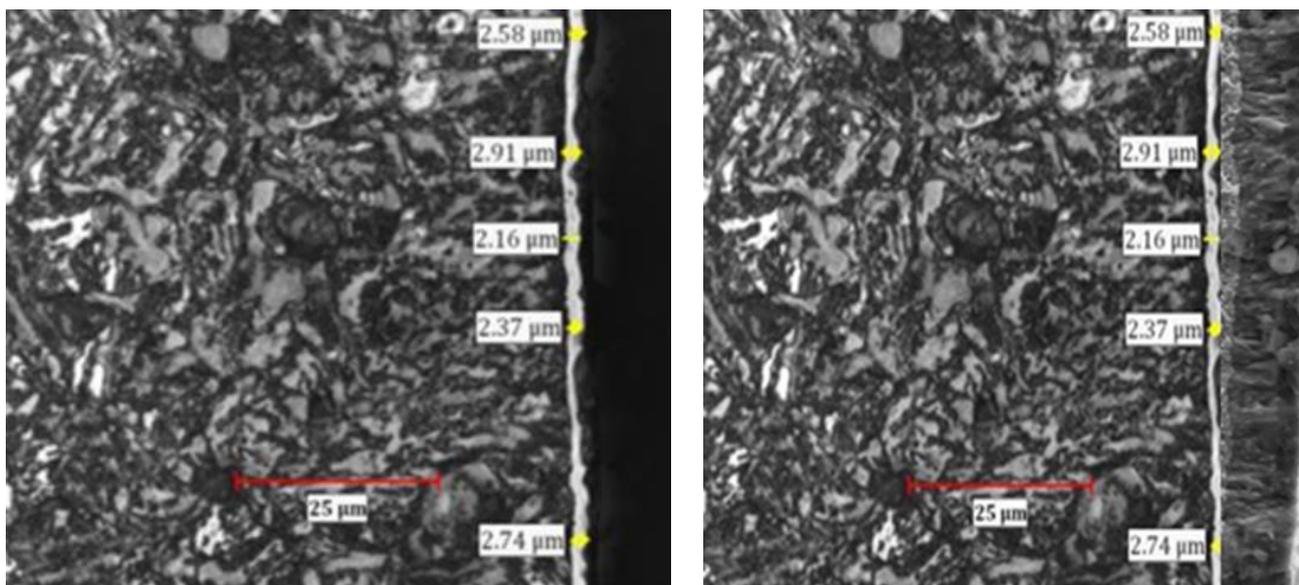
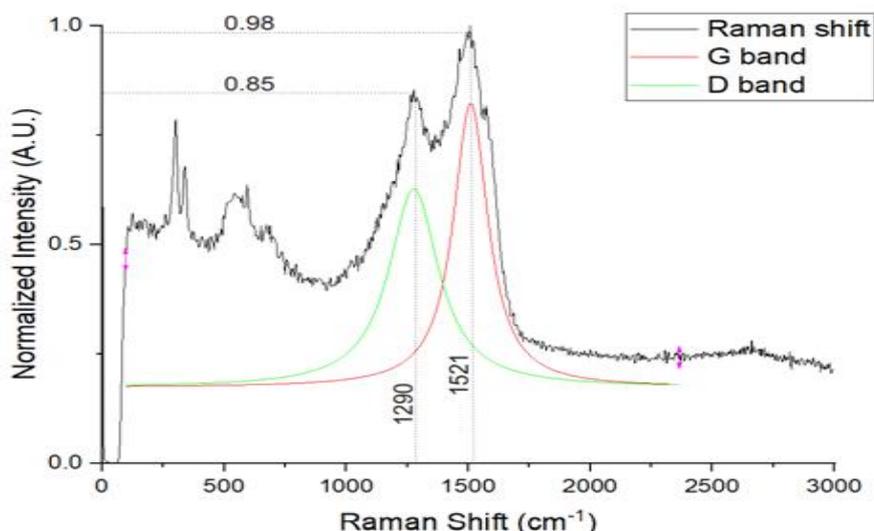


Fig. 1 Coating morphology of DLC and Ni<sub>3</sub>Al coating on ZA-27 alloy

The Microstructure of the Substrate with DLC and Ni<sub>3</sub>Al coating were observed under Nikon Microscope LV150N with Clemex Image analyser. The micrographs reveals that the DLC and Ni<sub>3</sub>Al coating formed on substrate surface has uniform thickness throughout the surface as shown on Fig. 1. In DLC, near the surface of the coating there are more of carbides in the ferrite matrix and less number of plate like structure called bainite which are formed due to the hardening of the substrate at high temperature and quenching at lower temperature. In Ni<sub>3</sub>Al intermetallic compound has  $\gamma'$  phase, which harden the matrix materials.

### 3.2 Raman spectroscopy analysis



**Fig. 2 :** Raman Spectra of DLC coated on Za-27 alloy.

After deconvoluting the curves, the resultant Raman spectra were fitted using two Gaussian function curves. One of the peaks is at wave number 1360  $\text{cm}^{-1}$ , which corresponds to the D peak of the  $\text{sp}^3$  Carbon bond. The breathing modes of the  $\text{sp}^2$  atoms in rings are responsible for the D peak. The G peak, which corresponds to the  $\text{sp}^2$  carbon bond and is positioned at wave number 1550  $\text{cm}^{-1}$ , is the second peak. The G peak is caused by  $\text{sp}^2$  atoms extending their bonds in rings and chains. The ratio of  $\text{sp}^2$  and  $\text{sp}^3$  bonds in the coating is proportional to the intensity of D (ID) and G (IG) peaks. The  $\text{sp}^2$  site configuration is linked to the G peak and ID/IG. The  $\text{sp}^2$  sites are placed in rings when the G peak intensity is low and the ID/IG ratio is high. When the G peak intensity is low and the ID/IG ratio is low, the  $\text{sp}^2$  sites are arranged in chains. Fig. 2 shows the Raman spectra of the DLC coating.

It is observed from the raman spectra that the G peak is located at 1521  $\text{cm}^{-1}$  and D peak is located at 1290  $\text{cm}^{-1}$ . The Corresponding intensity of the G peak is 2049 and D peak is 1862. and Normalized intensity of the G and D peak are 0.98 and 0.85 respectively. According to Ferrari and Robertson[13], the nature of the coating is amorphous carbon coating with hydrogen content (a-c:H) if the G peak is located between 1500 and 1530  $\text{cm}^{-1}$ . The G peak in the obtained Raman spectra is positioned at 1521  $\text{cm}^{-1}$ , indicating that the DLC coating is a-C:H. The main impact of the H in a-C:H DLC coating is to saturate the C=C bonds as  $\text{CH}_x$  groups. The H-bond (hydrogen) binds the majority of the  $\text{sp}^3$  sites. The ID/IG ratio of the obtained Raman spectra for DLC coating is found to be 0.85, and they have summarized experimental data from various sources and have shown that  $\text{sp}^3$  content in the hydrogenated DLC is related to G-peak position (WG) in the films. Empirical relation was obtained by fitting the data points between the wavelength of 1525  $\text{cm}^{-1}$  and 1580  $\text{cm}^{-1}$  which is given in the equation (1) thereby calculating the  $\text{sp}^3$  content using the above equation for the wavelength of 1521  $\text{cm}^{-1}$  was found to be 0.52 .

$$\text{sp3 content} = 0.24 - 48.9 (\text{WG} - 0.1580) \dots\dots\dots(1)$$

### 3.3 Wear results

#### 3.3.1 Influencing of sliding distance

Fig. 3 shows the plot of wear against time from the experimental data of the DLC coated and Ni<sub>3</sub>Al coated ZA-27 alloy. In Ni<sub>3</sub>Al coated the material wear increases with increase in time, whereas for DLC coated sample the material wear gets constant after some period even with increase in the time duration. The average wear of the Ni<sub>3</sub>Al coated was 46.28 microns and of DLC coated sample was found to be 26.47 microns. Fig. 3(a) shows the wear at speed of 100 rpm, DLC graph shows initially very low upto 200 m and then it slowly increasing with sliding distance then it maintain 300 mm to 600 mm at constant wear then it drastically increases due to loss of coating materials. The coating material loss its grip at 600 mm in the case of DLC but in the case of Ni<sub>3</sub>Al it loses at 200 mm at lower speed. In the case of 200 rpm speed the signature of DLC shows almost same from 200 m to 1000 m. But the curve of Ni<sub>3</sub>Al is higher in wear compared to 100 rpm, shown in Fig. 3(b). The partial surface area gets in contact with disc materials hence it shows higher wear rate. In Fig. 3(c) the huge difference between DLC and Ni<sub>3</sub>Al was observed. The Ni<sub>3</sub>Al coatings initially worn out on only surface in contact with disc at higher speed, hence it shows huge wear after 200 m travel of the disc. But on the other hand the DLC is shows nominal wear around 20 micron same as 200 rpm and even 100 rpm speed, due to its stable coating nature.

#### 3.3.2 Influencing of Wear load

The influence of wear load on the wear rate for both DLC and Ni<sub>3</sub>Al coatings is shown in Fig. 4. The applied load is directly proportional to wear load. At higher load, the pressure increases the abrasion, which leads to an increasing wear rate of the coated specimens. The higher load increases the shear strain, which creates shear deformation of the mating surface. Some researchers [14&15] have observed that the increase wear rate with increasing wear load for coating specimens. The higher wear rate is the contribution of breakage of coating and removal of base materials from the ZA-27 alloy. one more reason for higher wear at higher load increases the interfacial temperature of the coating and disc results thermal softening of the coating material and higher the removal rate.

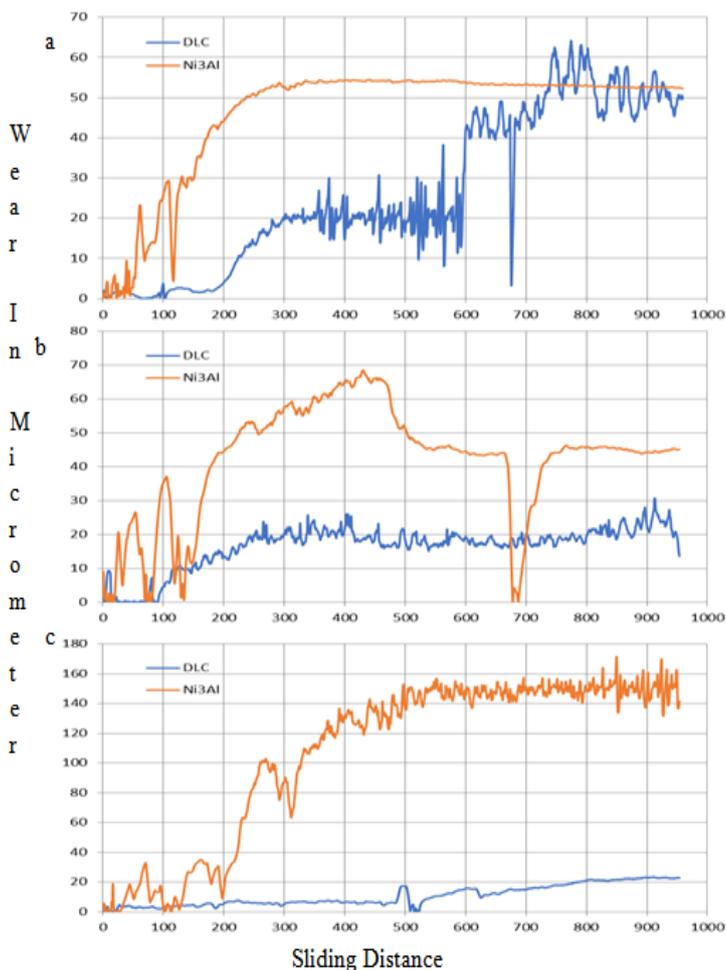


Fig. 3 Wear function of di

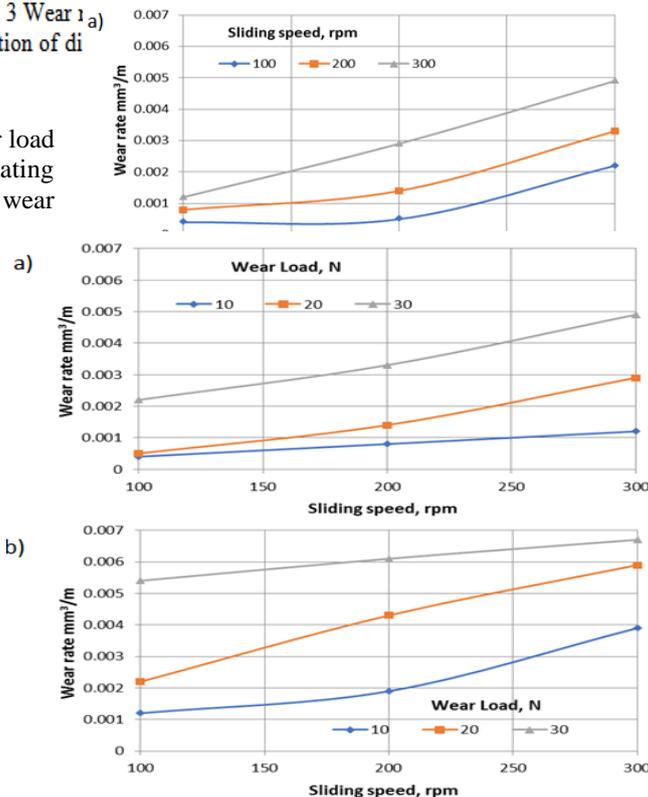


Fig. 5 Wear rate of a) DLC and b) Ni<sub>3</sub>Al coating on ZA-27 alloy as function of Sliding distance for different loads at constant sliding distance of 1 km

### 3.3.3 Influencing of sliding speed

Fig. 5 shows the wear rate as a function of sliding speed for different wear loads at sliding distance of 1 km for both DLC and Ni<sub>3</sub>Al coatings. Irrespective of the coating, the wear rate increases with increasing sliding speed of the wear disc. The higher wear rate was seen in higher sliding speed due to vibration of pin on the disc during sliding leads to large amplitude impact on the specimens. At higher temperature developed at the mating surface leads to thermal softening and also delayering of coating layer from the host material because of difference in thermal coefficient of both host and coating materials

### 3.3.4 Influencing of Coating Materials

Fig.6 shows the wear rate of DLC and Ni<sub>3</sub>Al coated on ZA-27 alloy. The graph shows that the addition of DLC particles significantly increased the wear resistance hence a lower wear rate of order of 0.0004 mm<sup>3</sup>/m was observed but in the case of Ni<sub>3</sub>Al coating order of 0.003 mm<sup>3</sup>/m was observed. The superior hardness of the DLC coating that is 16 to 24 GPa is one of the influencing parameters on wear resistance compared to Ni<sub>3</sub>Al of hardness of 2.452 GPa. Previous researchers showed that the mating surfaces for DLC coated specimens showed that formation of the graphitized layer acts as a self-lubricating hence reduces both friction and wear rate.

### 3.4 Friction coefficient

#### 3.4.1 As a function of sliding distance

The influence of sliding distance on coefficient of friction for different loads at constant speed of 100 rpm is shown in Fig. 7. The range of coefficient of friction of different coatings is 0.05 to 0.35. In the case of DLC coating it ranges from 0.05 to 0.15 due to graphitization at the mating surface. On the contrary, the Ni<sub>3</sub>Al shows the variation of 0.1 to 0.33 due to the hard and brittle in nature of the materials. The friction curves are in zig-zag in pattern due to vibration and slipping of the pin on the disc. The higher the slip the greater oscillation was observed in the curve.

#### 3.4.2 As a function of wear load

The Fig. 8 shows that the variation of coefficient of friction as a function of DLC and Ni<sub>3</sub>Al coating specimens. The coefficient of friction increases with increasing wear load irrespective of the coatings because of the change in shear rate. Due to continuous vibration of the pin and rubbing against the disc at higher load it increases the temperature and plastic deformation of the specimen and in turn leads to destruction of the wear surfaces and reduces the area of contact, damage the oxide layer that leads to higher roughness surfaces and hence higher coefficient of friction.

#### 3.4.3 As a function of wear speed

The Fig. 9 shows the coefficient of friction as a function of sliding speed for different loads at constant sliding distance of 1 km. The results shows the average friction of both materials not significant difference with sliding speed for the both coatings. Increase of sliding speed changes the pattern of shear strain leads to change in mechanical properties of the mating surfaces. The mechanical strength of coating materials have higher shear strain [16] which leads reduce the area of contact hence there is no significant variation in frictional coefficient.

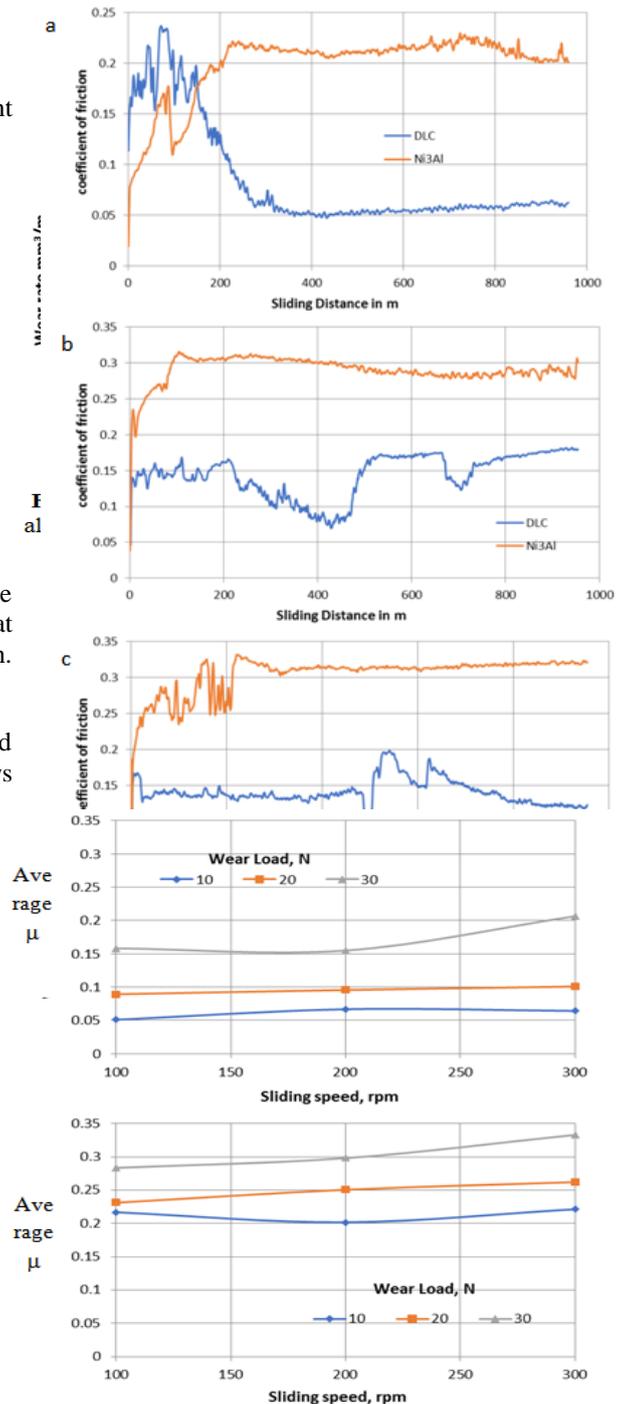


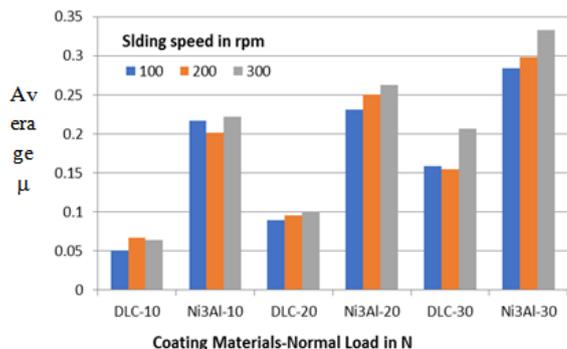
Fig. 9 Friction coefficient of a) DLC and b) Ni<sub>3</sub>Al coating on ZA-27 alloy as function of Sliding distance for different loads at constant sliding distance of 1 km

### 3.3.4. As a function of coating materials

Fig. 10 shows the effect of coating material type on coefficient of friction of the coated ZA-27 alloy. DLC coated specimen's exhibit lower coefficient of friction due to its self-lubricating and higher hardness compared to Ni<sub>3</sub>Al coatings. One more reason for lower friction is low level of surface roughness (very high smooth) that reduces the chance of abrasion at counter surface. Some researchers showed that DLC coatings have self-healing against the scratches that leads to reduction in the friction coefficient.

### 4. Conclusion

The PACVD process is being used to deposit a DLC and Ni<sub>3</sub>Al coating on an ZA-27 alloy specimens and are tested for wear and friction. The microstructure analysis clearly shows DLC coating formed on substrate surface has uniform thickness throughout the substrate. From Raman Spectroscopy analysis, it is observed that the deposited diamond like carbon coating was a hydrogenated amorphous carbon (a-C:H) coating because the G-peak is located at 1521 cm<sup>-1</sup> with sp<sup>3</sup> content of around 20%–30%. The wear of Ni<sub>3</sub>Al and DLC coating specimen showed 65 micron and 15 micron respectively similarly the frictional coefficient showed the range 0.05 to 0.35 for Ni<sub>3</sub>Al and 0.05 to 0.15 for DLC coatings. Both wear and frictional coefficient increases with increasing wear load but less significant variation was observed in the case of sliding speed.



**Fig. 10** Friction coefficient of DLC and Ni<sub>3</sub>Al coating on ZA-27 alloy as function of Sliding distance and load at sliding distance of 1 km

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