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Corrosion and cavitation erosion properties of sub-micron WC-Co /Cr_3C_2-NiCr multi-layered coating on aluminium substrates

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Abstract

Marine and automobile components are subjected to corrosion and cavitation erosion during their service. This paper aims to study the use of hard coatings on aluminium substrates with multiple layers of coating comprising of sub-micron sized WC-Co and Cr_3C_2-NiCr for enhancement of hardness, corrosion and cavitation erosion properties. Coatings are applied on aluminium substrates using high-velocity liquid fuel (HVLF) spray technique and the coating parameters are optimized for best results. The results indicate that multiple layered coating with alternate film coatings of Cr_3C_2-NiCr & submicron WC-Co has significantly improved the hardness of aluminium surface. The resistance to corrosion with multiple layers of coating is found to be exceptional and similar to monolayer Cr_3C_2-NiCr coating. Cavitation erosion tests performed as per ASTM G32 show that coating with multiple layers could resist the erosion of materials under dynamic conditions. The number of layers in the multiple-layer coatings strongly affects the hardness, corrosion and cavitation erosion properties.

1. Introduction

The cast-iron and steel components of IC engines or marine components can be replaced with aluminium parts to reduce their weight significantly. Although aluminium possesses a better heat transfer coefficient, its main drawback is low wear resistance. This predicament limits the scope of using aluminium for the IC engine and marine components. However, by making the aluminium more resistant to wear and by increasing its hardness, it can be used in multiple parts of the automotive engine and marine applications. There are many ways of improving the hardness and wear properties of aluminium by making metallurgical changes such as anodizing, heat treatment, etc. and also by alloying. The other method of improving the properties of aluminium is by using hard coatings that can significantly enhance the hardness thereby improving wear characteristics of the aluminium surface.

Coating with composites of ceramic and metallic materials also called cermet coatings like tungsten carbide with binder material cobalt (WC-Co in 88:12 ratio) and chrome carbide with nickle chrome as a binder (Cr_3C_2-NiCr in 75:25 ratio) had been widely used as thermal spray coatings in automotive and marine industries. Numerous researchers [1-31] investigated the phenomenon of enhancement of hardness and tribological properties of aluminium surfaces coated with diverse types of materials. Materials such as alumina (Al_2O_3), titania (TiO_2), tungsten carbide-cobalt (WC-Co) (88:12), chrome carbide-nickel-chrome (Cr_3C_2-NiCr) (75:25) and the combination of several metallic & ceramic materials have been widely researched as coating constituents.

1.1 Cavitation erosion of marine components

Marine components function under challenging environments due to their encounter with both salt and freshwater, which are corrosive, which is the main reason for the degradation of marine components. The major cause of failure of marine parts is cavitation erosion which is regularly detected in all fluid machinery. Cavitation erosion is an occurrence in which vapor bubbles forming inside a liquid impinge on a metal surface, resulting in the removal of the material. Under cavitation erosion, the substrate is exposed to dynamic fluctuating loads with velocities nearing a few hundred meters per second badly affecting the surface. Hong et al. [10] examined the effect of cavitation erosion on the eroding performance of WC-10% Co-4% Cr coating. They found that the coating was less affected due to corrosive invasion under cavitation erosion compared to substrate materials. Some studies by Krella et al. [14] show that multilayer coatings are more resistant to cavitation erosion compared to monolayer coatings.

Further, as the layers increase beyond a specific limit, there will be deterioration in the cavitation corrosion. This was found to be due to the weakening of the coating bond, owing to a decrease in coating thickness with severals coating layers increase. Peat et al. [17] studied three coatings Viz., tungsten carbide, chromium carbide, and aluminium oxide deposited by high-velocity oxy-fuel technique. Investigations made in slurry erosion and dry erosion conditions show that WC-Co is the best choice of coating for resistance to cavitation erosion with chromium carbide failing the test.

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1.2 Present investigations on multi-layered coating

Srinivas et al. [23] in their earlier work, investigated the mechanical and tribological properties of aluminium substrates with multi-layered coatings. From the fore mentioned studies, it can be observed that although Cr_3C_2-NiCr coatings are the best choice for automotive and marine applications due to its resistance to high-temperature corrosion and excellent oxidation protection. Nevertheless, their main drawback is inferior hardness resulting in lower resistance to wear than expected. As a replacement to Cr_3C_2-NiCr coatings, researchers investigated tungsten carbide-cobalt (WC-Co (88:12)) coatings which possess greater hardness and excellent wear resistance. They found that WC-Co coatings are ineffective at temperatures above 450ºC.

These investigations intend to explore the possibility of multi-layered coating with alternate layers of Cr_3C_2-NiCr (75:25) and WC-CO (88:12). A multi-layered coating contains alternative layers of two dissimilar materials that can embody the advantages of both materials and complement the drawbacks by minimizing the defects in adjacent layers in the coating thereby improving hardness resulting in better wear protection. Further, the interchanging layers have a different thickness which can endure high operating pressures to maintain performance without disintegrating. A multi-layered coating can consist of 3 to 5 number of individual layers to tune the desired properties. However, too many layers beyond 5 would decrease the thickness of individual layers rendering multi-layer coating useless. Cao et al. [4] investigated hardness and wear properties of Ni/Al multi-layer coatings and found that due to the manifestation of the semi-coherent boundary, the micro-hardness of Ni/Al multi-layers is much higher than pristine Ni monolayer coating resulting in better tribological properties.

The present study is made with multi-layered coatings of 1, 3 and 5 layers of coatings containing alternating filmy layers of Cr_3C_2-NiCr &WC-Co with Cr_3C_2-NiCr as the top layer. The studies are made in terms of improvements in porosity, micro-hardness, the adhesion strength of coating, corrosion and cavitation erosion. The effect of the number of layers of coating on hardness, corrosion, cavitation erosion wear has also been investigated. These studies could be a step ahead in the commercialization of multi-layered coatings on aluminium substrates for intended use in internal combustion engines and marine applications.

2. Experimental

In the current investigations, aluminium (light metal 9 grade) is chosen as the base material. The Coating materials are WC-Co (88:12) and Cr_3C_2-NiCr (75:25) agglomerated and sintered powders purchased from M/s Inframat Corporation.

The loose agglomerates of micro-sized Cr_3C_2-NiCr and nanostructured WC-Co particles can be seen in Figure 1. The materials are coated on aluminium substrates by high-velocity liquid fuel (HVLF) spray technique.

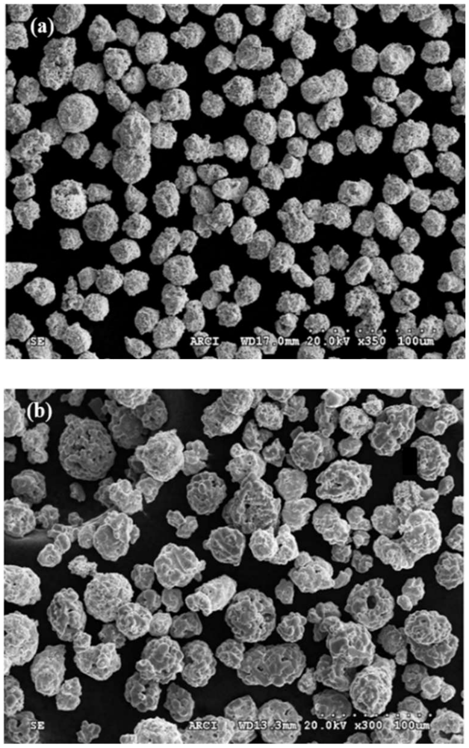

Figure 1. HRSEM image of agglomerated powders (a) WC-Co (88:12) and (b) Cr_3C_2- NiCr (75:25)

2.1 Coating procedure using HVLF spray technique

Before coating, the surface of the specimen was grit blasted to facilitate immediate attaching of coating material to the substrate, thereby reducing the cracks on the boundary leading to higher adhesion strength of the coating. The specimens are placed in a grit blast furnace, and grit blasted using dry air and alumina particles of 24 grit size. To remove moisture content, powders were preheated in an oven and then loaded into the HVLF gun for spray coating.

In HVLF thermal spray process, oxygen and liquid fuel are burnt using an ignited torch after which the byproducts of combustion reach a temperature of 2700ºC. The coating material is injected through the flame, which becomes molten particles and will be projected on to the specimen at velocities in the range of 2000 $m \cdot s^{-1}$. The materials get deposited on the substrate as liquid form, gets cooled and solidifies. But the process involves a combination of heat and velocity so the material gets heated up and deposits as individual particles thereby leaving little chance of fusing of particles.

Accurate control of all spraying parameters like powder feed rates, the position of the gun, enables better quality coatings.

Table 1. Optimized coating conditions for spraying

Method of coating		High-velocity liquid fuel spraying
Fuel used		Aviation turbine fuel
Gas parameters		
Gas pressure	Pressure, Bar	Flow, lpm
Oxygen	11±0.2	240±10
Nitrogen	7.5±0.2	400±5
Pressure of fuel	8.5±0.2	65±10
Powder feed parameters		
Feed rate of powder during spraying		40 ±0.2 $g \cdot min^{-1}$
Spray distance		7 inch
Rate of traverse		0.04 ms^{-1}

Coating properties and chemical composition are strongly affected by thermal spray process parameters [1]. The porosity, hardness and cavitation erosion resistance of the coating is also affected by all these parameters. Numerous coating experiments were done and coating parameters were optimized to achieve the best properties. The coating parameters for best results are as tabulated in Table 1. In case of multi-layered coatings, initially Cr_3-C_2-NiCr is coated on the surface and the coating was allowed to cool. The coating is grit blasted and next coated with W-Co layer. Likewise 3 layers and 5 layer coatings were carried out with Cr_3-C_2-NiCr as the top layer.

During coating process, it is challenging to control the thickness of the layer. Hence the layers were coated with higher thickness than required and then polished to the required thickness. The discs are coated to a thickness of 300-350 μm during experimentation and after coating, the specimens are carefully washed to take out the byproducts of combustion. The sample is polished to a thickness of 240-275 μm to obtain the surface finish suitable for application in marine and automotive components. Heat treatment is conducted on the coated specimens in an argon atmosphere at 400°C.

2.2 Microhardness of coatings

Microhardness indicates the resistance of the surface to deformation and wear. The microhardness test is done as per ASTM E 384. In the current study measure, microhardness is measured at an applied load of 200 gf with indentation don at 10 different locations on the coating and taking the hardness of the average value.

2.3 Electrochemical corrosion tests

An Electrochemical corrosion test assesses the resistance of aluminum alloys and coatings in resisting corrosion. The corrosion resistance is assessed in terms of electric corrosion potential measured during a potentio-dynamic polarization test conducted as per ASTM G 69. This study can also estimate the behaviour of the coated specimen during pitting corrosion. In this test, the electric corrosion potential of the material is measured by exposing the surface of the material to an aqueous solution of 3.5% sodium chloride (NaCl) solution mixed with hydrogen peroxide which serves as the cathodic reactant. The initial potential is fixed at -0.25 V (OC) and at 0.166 mVs^{-1} the SCE potential scan was carried out until the final potential of pitting is arrived at.

2.4 Cavitation erosion test

Cavitation erosion test is conducted on the samples using an ultrasonic method as per ASTM G 32 standard. The analysis is carried out in distilled water maintained at 25°C under an ultra-sonic frequency of 20 kHz. The graphic of the test setup is presented in Figure 2.

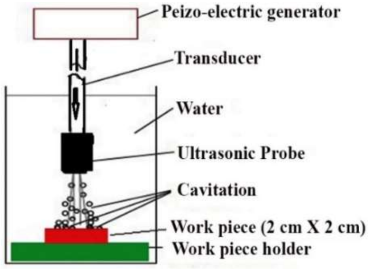

Figure 2. Schematic of cavitation erosion test set up

In this test, the coating area is placed in a water bath and a 20-kHz ultra-sonic probe tip is placed over the surface at 1 mm distance. The ultrasonic probe generates longitudinal ultrasonic vibrations that are transferred into the liquid medium as ultrasonic waves consisting of a series of expansions and compressions. These pressure variations strongly separate the liquid molecules producing microbubbles that collapse aggressively on the surface of the sample. These implosions produce shock waves creating extremes in pressures and temperatures on the surface, activating cavitation erosion.

Before the start of the test, the coated sample is weighed and immersed in a container of distilled water. Initially, the test is done for 30 min and after completion of the test, the sample is removed, washed with water and dried in a vacuum oven. The weight of the specimen is noted down after drying. The test is carried out for a total duration of 10 h and measurement of weight is carried out at a frequency of 30 min to obtain data of mass loss concerning time. The relative mass loss of samples with time is compared to assess cavitation erosion resistance.

3. Results and discussion

3.1 Characterization of composite

The coated specimens were carefully cut using a cutting tool with a diamond tip and a metallographic impressed coated sample of size 10 x 10 mm was prepared to characterize the microstructure of the coating. The SEM images portraying the cross-section of the coating were recorded under potentials of 15 kV and 30 kV and shown in Figure 3 and 4. The figures show a dense and consistent microstructure of coatings with a porosity range of 1-2%. Due to optimized coating parameters, the boundary between Coating and base material seems to be free from micro-cracks indicating good adhesion between the coating and the substrate. This was realized due to the high kinetic energy attained by the coating material during the coating process, which ensured an excellent solidity in all the coatings creating carbide-based coating surface with least porosity. The HRSEM micrographs also depict the uniform spreading of carbide particles in the coating.

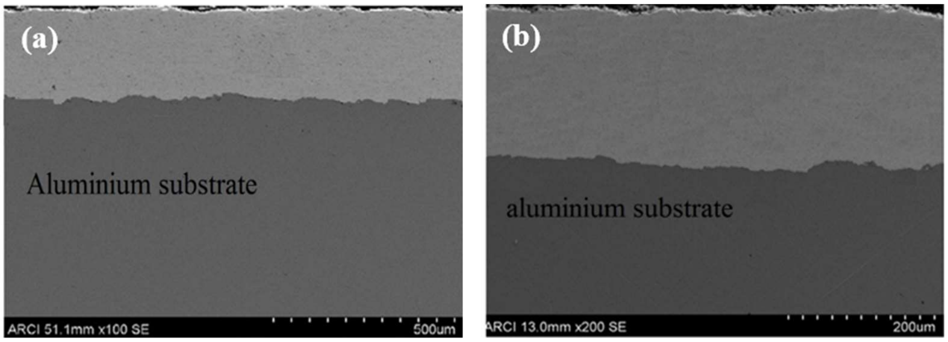

Figure 3. HRSEM micrographs of monolayer coating on the aluminium substrate (a) Cr_3C_2-NiCr (75:25) and (b) WC-Co (88:12).

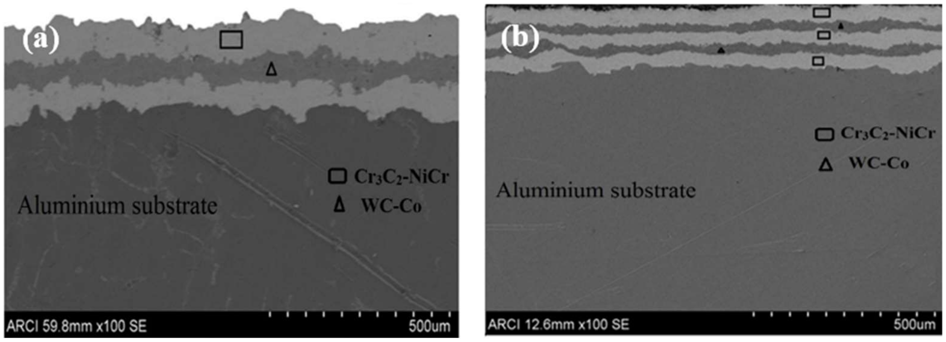

Figure 4. HRSEM micrographs multi-layered coating with alternate layers of Cr_3C_2-NiCr (75:25) and WC-Co (88:12) on the aluminium substrate (a) 3 layered coating (average layer thickness: 60 µm) (b) 5 layered coating (average layer thickness: 27 µm)

3.2 Porosity and microhardness of coatings

Microhardness correlates directly to the strength of the coating. The hardness of the coating is closely related to its porosity and value of porosity lower than 1% indicates good hardness. A higher value of porosity will result in the reduction of the hardness of coating, which will lead to cracks in the coating. The porosity micrographs of coatings are shown in Figure 5. The result of porosity from the micrographs shows that the Cr_3C_2-NiCr sample has higher porosity compared to all other samples. When it comes to multi-layered coating, as the number of coating layers increases the porosity decreases and the best porosity is observed for coating owing to the reduced size of the coating particles.

The porosity of all the coatings measured using a metallurgical microscope is reported in the Table 2

A hardness value between 500 to 800 HV is crucial for the application of coatings in IC Engines and marine components. The results of the microhardness test conducted as per ASTM E 384 are tabulated in Table 3. The standard deviation of the values is ensured to be within ±5%, which is acceptable as per standard. The results of the microhardness of the test samples show WC-Co has the highest microhardness of 1420±55 HV compared to all other samples whereas Cr_3C_2-NiCr shows the slightly less micro hardness 1015±45 HV. From the above results, it can be witnessed that when several layers of Cr_3C_2-NiCr and WC-Co are coated on the aluminium surface, there is a significant improvement in hardness because of the grouping of materials.

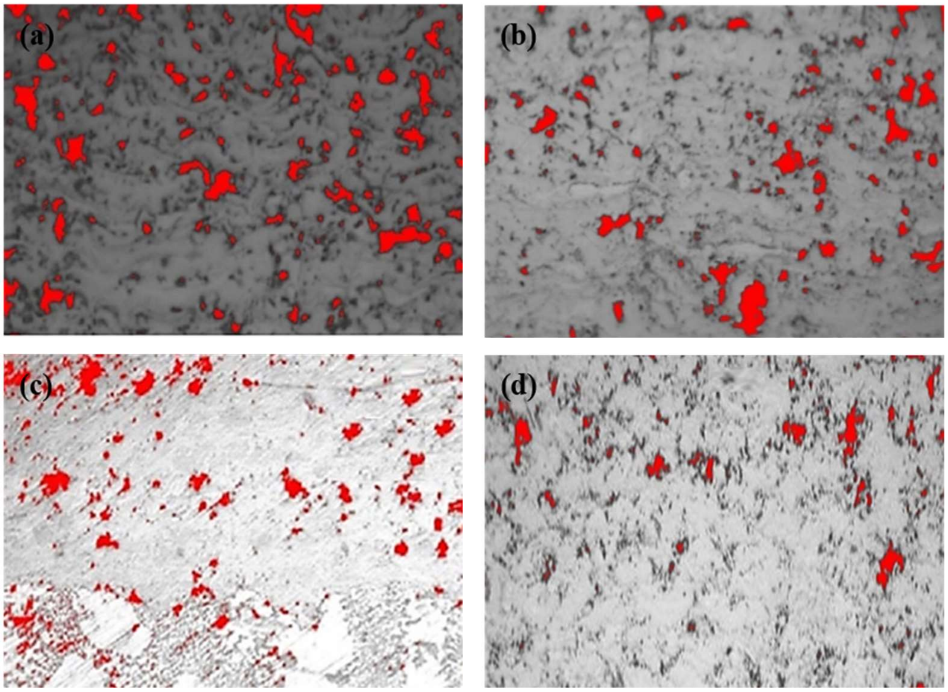

Figure 5. Porosity micrographs of coatings (a) Cr_3C_2-NiCr (75:25) (b) 3 layered coating (c) 5 layered coating and (d) WC – Co (88:12)

Table 2. Porosity values of the test specimen

Specimen	Coating thickness (μm)	Porosity (%)
Monolayer Cr_3C_2-NiCr (75:25)	253	1.71±0.25
Multi-layered coating (3 layers)	274	1.62±0.15
Multi-layered coating (5 layers)	244	1.15±0.11
Mono layer WC-Co (88:12)	231	0.98±0.12

Table 3. Microhardness values of the test specimen

Specimen	Coating thickness (μm)	Microhardness (HV)
Monolayer Cr_3C_2-NiCr (75:25)	253	1015±45
Multi-layered coating (3 layers)	274	1255±50
Multi-layered coating (5 layers)	244	1388±48
Monolayer WC-Co (88:12)	231	1420±55

In the case of multi-layered coating, the number of layers over the aluminium substrate has a profound effect on the hardness due to the decrease in the porosity as the number of layers increase. This decrease in porosity resulted in a denser coating that promotes hardness. With 3 layers and 5 layers of coatings, there is an improvement in hardness by 23.5% and 36.7% compared to Cr_3C_2-NiCr (75:25) monolayer coating. The hardness and porosity of the multi-layered coating with 5 layers are nearer to monolayer WC-Co (88:12). The results of porosity and microhardness are comparable with Zhou et al. [31] who studied mono layered coatings with Cr_3C_2-WC-NiCoCrMo and Cr_3C_2-NiCr materials and concluded that less porosity would lead to higher hardness.

3.3 Electrochemical corrosion tests

During Electrochemical corrosion tests, the critical value of the potential at which current increases severely can be reflected as significant electric corrosion potential (E_{corr}). Specimens exhibit better corrosion resistance if it possesses relatively more potential. In Table 4, the critical electric corrosion potential (E_{corr}) values are given for all the coating tested.

Figure 6 gives the trend of corrosion potential with input current and it can be observed that Cr_3C_2-NiCr coated specimen shown good anti-corrosion behaviour followed by 5 layers graded Coating and WC-Co coating. The potential is highest for monolayer Cr_3C_2-NiCr (75:25) coating followed by multi-layered layered coating with 5 layers. The lowest potential is recorded for WC-Co (88:12) monolayer coating. The test specimens are characterized using a metallurgical microscope to determine the extent of damage done during the corrosion test. As seen from Figure 7(a)-(d); the specimen with Cr_3C_2-NiCr coating could resist corrosion with minimum damage with 5 layer coating performing on par with Cr_3C_2-NiCr. WC-Co specimen got severely corroded.

Table 4. critical electric corrosion potential (E_{corr}) values test specimen

Specimen	**E_{Corr} (mV)**
Monolayer Cr_3C_2-NiCr (75:25)	-510
Multi-layered coating (5 layers)	-540
Multi-layered coating (3 layers)	-595
Monolayer WC-Co (88:12)	-630

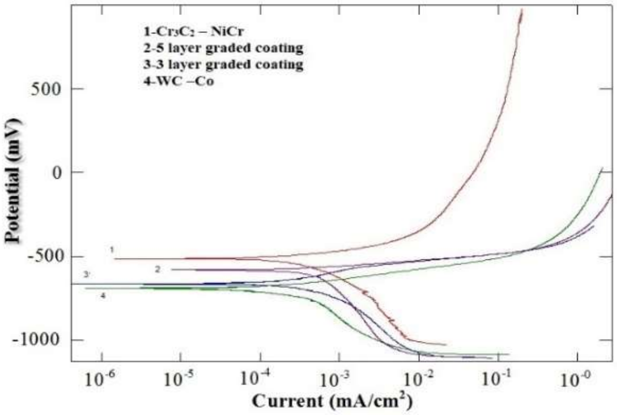

Figure 6. Variation of corrosion potential with an input current for coated.

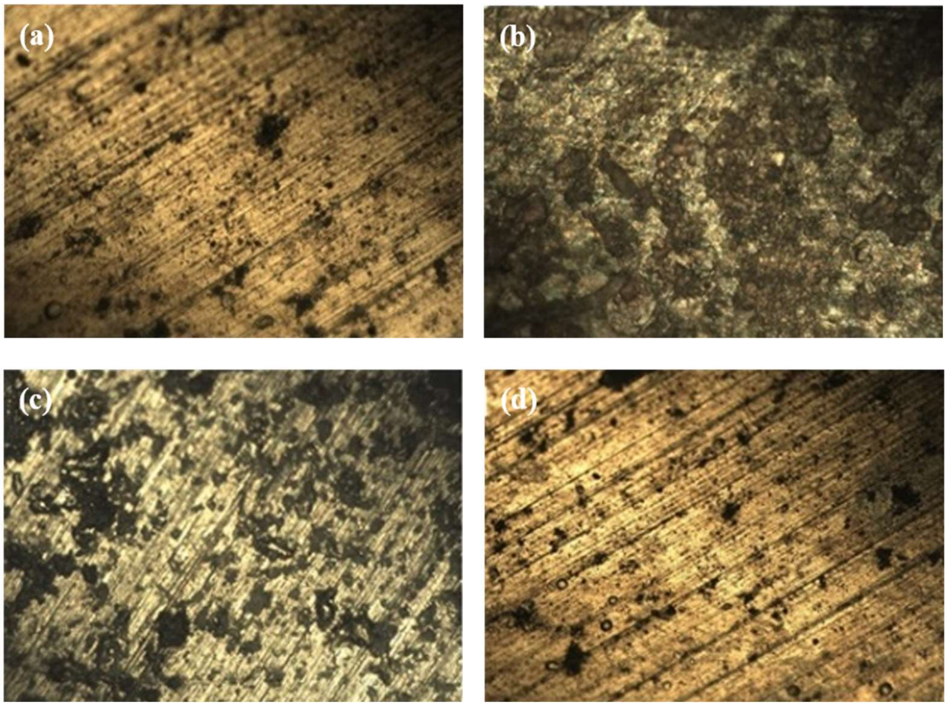

Figure 7. Micrographs of corroded surface (a) monolayer Cr_3C_2-NiCr (75:25) coating (b) monolayer WC-Co (88:12) coating (c) 3 layered coating and (d) 5 layered coating.

3.4 Cavitatin erosion test

Cavitation erosion resistance of test specimen is compared in terms of mass loss concerning the duration of the test in Figure 8, which shows a cumulative weight loss of test specimen over ten-hour periods. From the graph in Figure 8, it may be observed that the incubation period for mono layered Cr_3C_2-NiCr coating and 3 layered coatings is 30 min after which there is a sharp increase in the erosion rate characterized by acceleration period.

The acceleration rate continued till 4 h of test duration before the start of the deceleration of erosion wear loss.

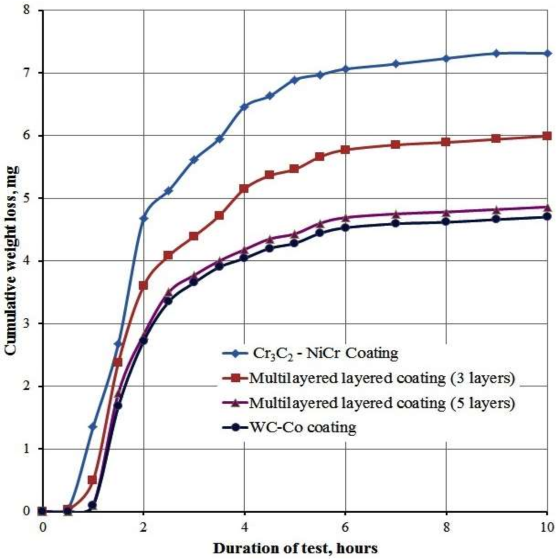

Figure 8. Graph showing cavitation erosion of test samples with time.

For 5 layered coating and WC-Co monolayer coating, the incubation period is longer at 1 h and the acceleration period after that is only up to 2.5 h. After the acceleration of the period, the slowing period and stable period of erosion wear loss were rapid, indicating higher cavitation erosion resistance of 5 layered coatings and WC-Co monolayer coating. WC-Co (88:12) coating possesses the highest hardness followed by 5 and 3 layers coatings with Cr_3C_2-NiCr (75:25) showing lowest hardness. The influence of layers in the multi-layered coating is found to be significant with an increase in erosion resistance observed with an increase in several layers. 5 layered coating displayed good erosion resistance and its performance is comparable with WC-Co (88:12) coating. The trends of cavitation erosion are found to be similar to that of studies reported in the literature [2,11,12,16].

Noting the results of the hardness test, it could be established that the multiple layers on the aluminium substrate gave substantial hardness to the coating, which ensued decreased erosion rate compared to single-layer Cr_3C_2-NiCr coating. Further, any increase in the number of layers in the coating to more than five would shrink the individual layer thickness below 40 μm which lessens the load-bearing capability of the coating and ultimately results in more erosion rates due to abrasion and plastic deformation. Moreover, the microstructure of the coating becomes loose with the increase in the number of layers because of decreased layer thickness which ultimately results in reduced crack resistance and adhesion between layers [28]. It can also be noted that although WC-Co (88:12) Coating performed well in cavitation erosion test, it could not perform well in the potentio-dyanmic corrosion test. The higher hardness could make it best in resisting cavitation corrosion. The multiple layers are thus advantageous in resisting both cavitation erosion as well as corrosion. The material Cr_3C_2-NiCr as the top layer is crucial to enhanced corrosion and erosion properties. Nickel and chromium resist corrosion and thereby giving it an edge over WC-Co coating.

4. Conclusions

The following conclusions can be made from the studies

1. Low porosity coatings were produced with good cohesion between the coating and substrate achieved with optimized the coating parameters.
2. The strength of chrome carbide-nickel chrome coating is found to have improved by coating WC-Co in alternate layers resulting in improved cohesion, reduction of porosity thereby better mechanical properties and enhanced microhardness.
3. Multi-layered coatings possessed low porosity and enhanced hardness with a good adhesion strength.
4. Multi-layered coatings possess resistance to corrosion is similar to that of Cr_3C_2-NiCr with WC-Co coating performing poorly.
5. The erosion resistance of five-layered coatings and WC-Co coating is found to be highest among all coatings characterized by a long incubation period and low acceleration stage owing to higher hardness.
6. The increase in the number of layers in multi-layered coatings plays a prominent role in enhancing the mechanical properties with 5 layer coatings giving the best results.
7. From the results of hardness, cavitation erosion and corrosion tests, it can be concluded that multi-layered coating with five layers possesses properties similar to WC-Co coating. Hence it can be implicitly concluded that multi-layered coating with Cr_2C_2 -NiCr as the top layer is also beneficial at high temperatures.

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