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TRIBOLOGICAL BEHAVIOUR OF NITRATE BASED ALLOY COATING ON EN 31 STEEL

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Abstract

Wear plays vital roles in many industrial applications have major issues resulting in failure, economic loss and personal injury. These properties are improved by surface coating. The principle aim of this study is to investigate the wear behaviour of Nitrate coatings on EN 31 steel substrate which is used for several applications in automotive components. For this purpose, AlCrN powder was Coated on EN 31steel substrate using a Physical Vapour Deposition technique (PVD). Fabricated layers will be characterized by using , scanning electron microscopy (SEM), Microhardness and Micro Abrasive tester.

The coating thickness is found to be 50 microns using Hermit scale through optical microscope. The coated area is found to have the formation of the steel microstructure with intermediate of Ferrite and Austenite with Carbide Particles. Carbide is hard material; as well as in situation like wear, where other metals would wear away but carbide has high quality of resistance.

Keywords — Micro hardness optical microscope, microstructure, hard material.

1 INTRODUCTION

Iron and steel are the most versatile, least expensive, and most widely used materials for construction of many engineering systems. They are unequaled in the range of mechanical and physical properties with which they can be endowed by alloying and heat treatment. Due to safety, economic, and environmental reasons, significant amounts of effort have been spent to extend the service life of machine components and structures. To meet these demands, various surface modification technologies have become major interest because they can provide superior surface properties such as high strength, thermal barrier, corrosion resistance, wear resistance, and fatigue resistance to structural materials.

1.1 Surface Technology

Surface technology means modification, structuring or coating of materials and components. In case of coatings, one may distinguish between „„„thick"" and „„„thin"" film technology. We shall talk about thick film technology for film thicknesses above 10 mm and thin film technology for film thicknesses between 0.1 nm and 10 mm. However, this division is not fixed.

According to the "Organisation Internationale des Constructeurs d"Automobile" (OICA) in 2007 around 53 million cars and 20 million commercial vehicles have been produced [1]. The automotive industry is one of the most important users of modern surface technologies.

In general surfaces are not perfect. However, in our daily life we communicate with objects mainly through their surfaces. Surface and coating technologies on one hand improve existing materials and products; on the other hand they are indispensable for the realization of innovative products based on particular properties of thin films.

1.2 Surface Engineering

Surface engineering involves the enhancement of certain properties of the surface of a component which are distinct from those of its bulk material. Wear and corrosion resistance are typical properties which can be improved by surface engineering (Mellor, 2006). There is a considerable effort on the part of research to develop techniques to impart improved wear and corrosion properties, to surfaces to improve component lifetimes resulting in less downtime for repair, thus it is cost effective. Surface engineering encompasses many and varied processes and techniques. These can be separated into three categories (Shipway, 2006).

1. Processes that modify the existing surface without a change in composition (e.g. transformation hardening, shot peening and surface remelting).
2. Processes that modify the existing surface by inducing a change in composition of the component, creating a surface engineered layer. Often this leads to a diffuse boundary between the substrate and the reaction layer, e.g. as in anodising, boronising and ion implantation.
3. Processes which apply a new material. As a coating, to the surface. i.e. those processed which lead to the formation of a different phase with a distinct boundary between itself and the substrate. Weld hardfacing, electroplating, thermal spraying, physical vapour deposition (PVD) and chemical vapour deposition (CVD) are examples of these processes.

Of these three categories, only 3 techniques in the third category have the capability of producing a thick coating in excess of 500 gm. Thick coatings are essential in some applications where high temperature, high wear resistance and/or corrosion resistance of components are of primary concern, such as landing gear, gas turbine components etc.

Thermal spray coatings have the potential to be alternative overlay-type coatings in a number of' circumstances. Thermal spraying can produce a coating with a low oxidation level, a low porosity and good adhesion. [1]

In addition, large surface areas and complex shapes can be coated with composite microstructures to suit particular service needs. Also thermally sprayed coatings can usually be applied without heating the substrate excessively, thus avoiding formation of a heat affected zone. A more detailed description of the thermal spray process will be given in the following sections.

1.3 Nitrate Based Coatings

In Wear, many industrial applications are major issues resulting in failure, economic loss and personal injury. To mitigate these problems, great efforts has been directed to acquire high performance coatings with improved mechanical and chemical properties based on Ni-based alloy, stainless steel, WC cermet and amorphous alloys in the past decades. Among the coatings, Nitrate based amorphous coatings are more attractive due to their unique properties including high hardness, superior corrosion and wear resistance and relatively low cost.

Nitrate based coatings are an attractive alternative to TiAlN, TiN due to an abundance of the natural resource (Fe) and its low material cost and good chemical and physical properties, such as high hardness of borides, low density, and reasonable thermal stability at elevated temperatures (Branagan et al., 2005; Liu et al., 2009)[3].

These coatings contain a Nitrate based matrix with a high chromium level to provide high hardness (carbide) which provides the wear resistance. Nitrate based alloys have been proposed for use for, wear resistance applications in various industrial fields such as aerospace industry, Automobile industry, etc. (Pang et al., 2002, Branagan, 2004; Mellor, 2006).

1.4 PVD Technique

The term physical Vapour deposition originally appeared in the 1966 book Vapour deposition by C.F.Powell, J.H. Oxley and J.M. Blocher jr.,(but Michael faraday was using PVD deposit coatings as far back as 1838) [1]. Physical Vapour deposition is a process that is currently being used to enhance number of products, including automotive parts wheels pistons, surgical tools drill bits, and guns.

Physical Vapour Deposition (PVD) technology consists of the techniques of arc deposition, ion plating, resistance evaporation, electron beam evaporation, sputtering and many others. It is used to deposit films and coatings or self-supported shapes such as sheet, foil, tubing, etc. The thickness of the deposits can vary from angstroms to millimeters. The application of these techniques ranges over a wide variety of applications from decorative to utilitarian over significant segments of the engineering, chemical, nuclear, microelectronics and related industries. Their use has been increasing at a very rapid rate since modern technology demands multiple and often conflicting sets of properties from engineering materials, e.g. combination of two or more of the following – high temperature strength, impact strength, specific optical, electrical or magnetic properties, wear resistance, fabric ability into complex shapes, biocompatibility, cost, etc. A single or monolithic material cannot meet such demand in high technology applications. The resultant solution is therefore a composite material, i.e., a core material and a coating each having the requisite properties to fulfill the specifications.

PVD technology is a very versatile, enabling one to deposit virtually every type of inorganic materials – metals, alloys, compounds and mixtures thereof, as well as some organic materials. The deposition rates can be varied from 10 to 750 000Å (10Å=1nm) per minute, the higher rates having come about in the last 25 years with the advent of electron beam heated sources [3].

The thickness limits for thin thick films are somewhat arbitrary. A thickness of 10 000Å (1µm) is often accepted as the boundary between thin and thick film. A recent viewpoint is that a film can be considered thin or thick [2].

The objective of deposition processes is to controllably transfer atoms from a source to a substrate where film formation and growth proceed atomistically. In evaporation, atoms are removed from the source by thermal means. Two methods of PVD are used, they are:

a) resistance (thermal) evaporation
b) electron beam evaporation

The physical Vapour deposition processes take place in vacuum. The vacuum environment is a complex one and is neither a void nor inert. To be successful, thin film deposition must be done with awareness of the effect of the environment upon the Vapour flux and growing film. The three most important aspects of the vacuum environment to thin film deposition are: the pressure, expressed as the mean free path, the partial pressure of reactive gasses and in inert working gasses and the film Vapour arrival to reactive gas impingement rate ratio.

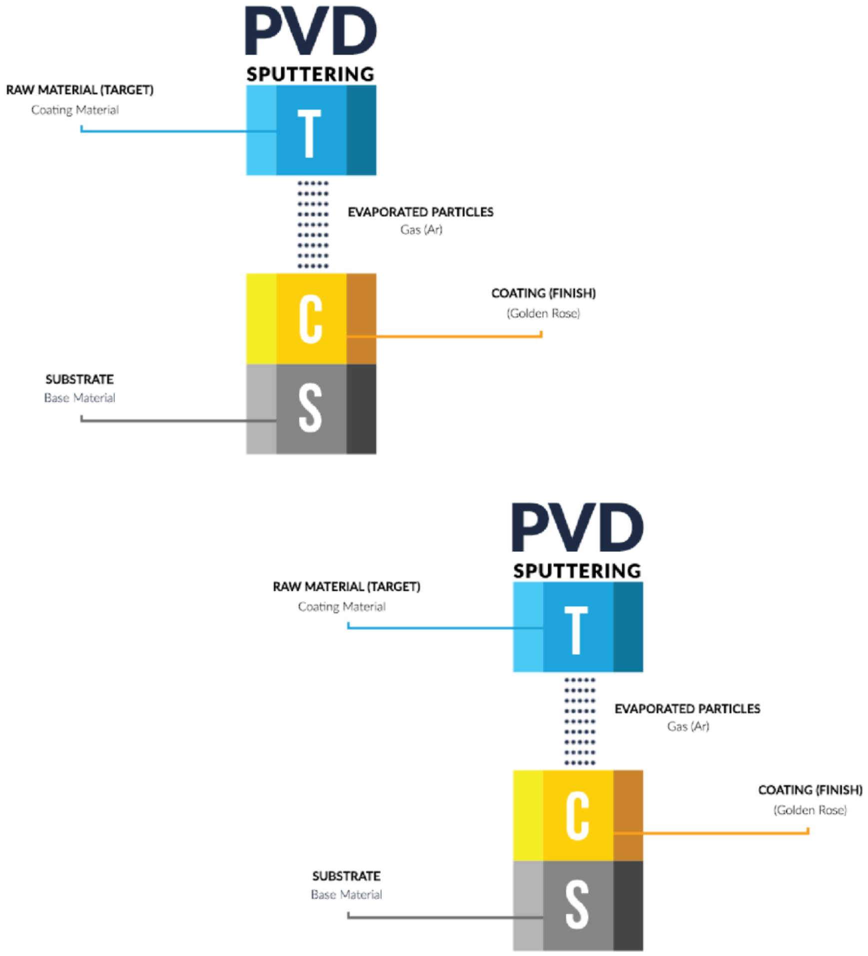

Fig 1.1 Process of PVD Technique

The current version of physical vapor deposition was completed in 2010 by NASA scientists at the NASA Glenn Research Centre in Cleveland, Ohio. This physical vapor deposition was made up of thin layer of metal that are bonded together through a rig that NASA finished developing in 2010. In order to make the coating, developer put the essential ingredients into the rig, which drops the atmospheric pressure to one torr (1/760 of our everyday atmosphere). From there, the coating is heated with plasma torch that reaches 17,540 degrees Fahrenheit. In automotive world, it is the newest alternative to chrome plating that has been used to trucks and cars of years. This is because it has been proven to increase durability and weigh less than chrome coating, which is an advantage because vehicle acceleration and fuel efficiency will increase.

2. LITERATURE REVIEW

2.1 Literature Review's On Nitrate Based Alloy Coating

M.S. Priyan (2008) have examined two commercially available gas atomized Al-Cr-N based alloy powders with different binder (e.g. Cr, Ni) and B contents namely Armacor M (compositions in wt% Fe-balance, 50%Cr-8.0%N-0.17%C-3.0%Si) and Armacor C (Fe-balance, 32.0%Cr-19.0%N-9.0%Co-4.0%Mo-2.4%Cu-4.0%B-0.12%C-1.4%Si in wt.%) [5]. These alloys are commercially available from Liquid metal Inc. It was reported that the Armacor M powder contained carbide and ferrite matrix phases whilst the Armacor C powder contained carbide and austenite matrix phase. This indicated that powders with different binder contents contain different matrix phase. However, the different B contents does not influence on the type of carbide phase.

Similar work by P. Hariharan(1997), the Armacor M (with compositions Fe-balance, 42.0%Cr-2.2%Si-6.1%N in wt.%) and Armacor C (with compositions 25.2%Fe-Cr balance-28.2%Ni-3.2%Cu-4.4%Mo-1.5%Si-4.3%B in wt.%) were analyze using XRD for both as received powders and physical vapour deposition. It is reported that the Armacor M powder consists of AL(Cr) solid solution matrix phase and Cr-rich metal[6].

The physical vapour deposition (PVD) based Armacor M coating has retained a Al (Cr) solid solution matrix phase and Cr-rich metal. But some oxide Fe2O3 inclusions were also present. The Armacor C powder consists of Al and Cr-rich metal carbide[7].

The physical vapour deposition (PVD) based Armacor M coating shown a higher hardness (6.49 GPa to 9.96 GPa) while the physical vapour deposition Armacor C coatings had a hardness (6.14 GPa to 7.54 GPa). This suggests a superior wear resistance of the physical vapour deposition (PVD) based Armacor M coating[3].

A.Ahmad (1999a) have characterized the microstructure of the Armacor M coating. A commercial Al-Cr-N based alloy; Armacor M was used to deposit the coatings using the physical vapour deposition(PVD).The microstructure of the cross-section of the coatings was revealed by SEM. Using backscattered electron imaging, two different phases present were seen as different contrast levels. Those phases were then identified as Al rich, Fe-Cr solid solution (the bright contrast area) and Cr-rich, chromium-iron carbide (the dark contrast area).The size of the boride phase in the coating was smaller than those found in the feed stock powder.

2.2 Researchers View's On Nitrate Based Alloy Coating For Wear Resistant

P. Hariharan (2001) has investigated wear behaviour of Armacor M coatings and Armacor C coatings deposited by plasma transferred arc weld-surfacing process. Pin-on-disc dry sliding wear tests were carried out using the pins of the Armacor M and Armacor C coatings against the disc made from SUJ2 steel with hardness of 2.01 GPa at a sliding speed of 0.8 m/s and total sliding distance 9048 m. It was reported that the plasma sprayed Armacor M coating had a higher wear resistance than the Armacor C coating. The high wear rate of the Armacor C coating was associated with a high friction coefficient.

P. Hariharan, (1997) have characterized the wear behaviour of Al-Cr-N based alloys systems. The Armacor M and the Armacor C coatings were deposited on the substrates using a physical vapour deposition(PVD). An abrasive wear test was employed using a rig based on the ASTM standard G65-91. The Armacor M coating had a higher hardness (6.5 to 9.96 GPa) than that of the Armacor C coatings (6.14 to 7.54 GPa). The Armacor M and the Armacor C coatings exhibited excellent wear resistance as compared with the physical vapour deposition. Inconel 625 coatings. The wear rate of the Armacor M and the Armacor C coatings was similar to Ni/Cr-Cr3C2 coatings, but higher than that of WC-Co coatings[5].

A comparison of the wear behavior of the Armacor M coating and the Armacor C coating which were sprayed with the physical vapour deposition using a TAFA JP5000 gun on mild steel substrates was reported by Manna et al. (2008). A ball-on-plate test was employed using alumina and hardened l00Cr6 balls. The high friction coefficient (1.0 against alumina ball and 0.97 against100Cr6ball observed for the Armacor C coating was associated with a high wear coefficient.

Zeng (2002) have characterized the wear behavior of the as-sprayed Fe63Cr8Mo2B5C5Si1Al4 (in at %) and heat treated plasma deposited coatings using a two-body abrasive wear test (ball-on-disk). A Si3N4 ball with a diameter of 0.5 inch and hardness of 15.4 GPa, was loaded against the coating with a sliding speed of 0.106 m/s. The investigations showed that no wear was found on both the as-sprayed and plasma deposited coatings.

The wear performance of the as-sprayed physical vapour deposition was conducted using a three-body wet sand rubber wheel wear test. The as-sprayed physical vapour deposition exhibited high resistance to wear (weight loss of 0.0795 g.) similar to that of the 1090N steel and after the coatings exhibited improved wear resistance (weight loss of 0.0201g).

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3. METHODOLOGY

3.1 Problem Defenition

Wear plays vital roles in many industrial applications are major issues resulting in failure, economic loss and personal injury. To mitigate these problems, great efforts has been directed to acquire high performance coatings with improved mechanical and chemical properties based on Ni-based alloy, stainless steel, WC cermet and amorphous alloys in the past decades. Surface wear have become the main reasons for equipment failure. The need for improving the qualities of surface leads to the development of surface modification techniques such as spraying, electroplating and laser or plasma cladding.

3.2 Research Objectives

The goal of this project work is to assess the microstructure, micromechanical properties and wear behavior of PVD based coatings manufactured using commercially available AlCrN alloy powders.

The first objective is to identify the microstructures formed in PVD based coatings using the commercially available AlCrN alloy powders. The techniques of X-ray diffraction (XRD), scanning electron microscopy (SEM), micro hardness testing and Wear testing were all employed to characterize powders and coatings.

The second objective is to investigate the lubricated wear property of coatings produced from the commercial powders. The sliding wear tests of the coatings were performed using micro abrasion wear test machine with EN31 steel ball.

4 EXPERIMENTAL PROCEDURE

The aim of this chapter is to provide a generalized introduction to the characterization techniques used in this work. A number of microstructural characterization techniques, such as X-ray diffraction (XRD), scanning electron microscopy (SEM), are then presented. The assessment of micro hardness of coatings and the procedure of Micro Abrasion Wear Test are briefly described.

4.1 Materials Selection And Preparation

AISI 52100 steel were used as a substrate material in the present study. The chemical composition of the substrate material is shown in Table 4.1. Suitable specimens (length 12 mm and diameter 25mm), were fabricated from the substrate bar by EDM wire cutting to a close proximity to the required size, followed by the grinding of both the faces, to remove surface irregularities as well as to deal with the consequences of any induced micro-level changes that might have occurred in the heat affected zone as a result of the EDM cutting.

All evaluated coatings were deposited in Staton Company. AlCrN coatings were deposited by ARC PVD method. Deposition time for all coatings was 30 min., specimens rotated, rotation speed was 4 - 5 rpm, and the specimen-cathode distance was 20 cm. The specimens were placed on one side horizontally so that deposition took place on one side only. Before the deposition substrates were cleaned by ultra-sonication in acetone and subjected to Arc plasma etching – P = 0.2 Pa, U = 1.2 kV, t = 20 min. and heating – P = 5 Pa, U = 1.24 kV, t = 60 sec.

Table 4.1 Chemical composition of the substrate

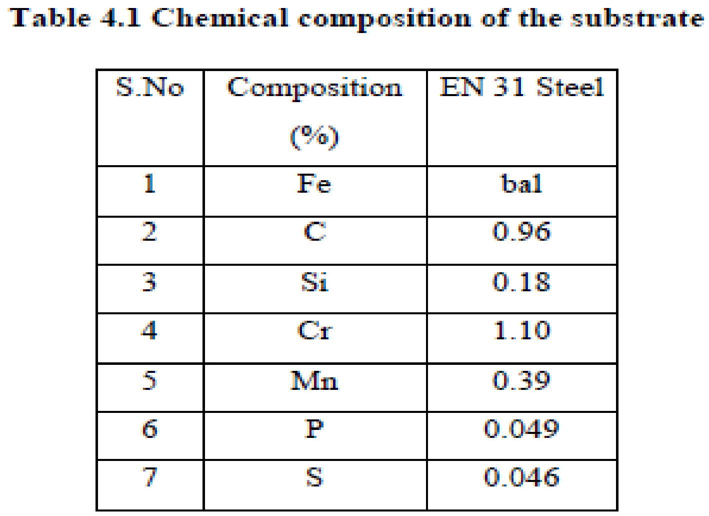

Table 4.1 Chemical composition of the substrate

S.No	Composition (%)	EN 31 Steel
1	Fe	bal
2	C	0.96
3	Si	0.18
4	Cr	1.10
5	Mn	0.39
6	P	0.049
7	S	0.046

Table 4.2 PVD parameters with AlCrN coating

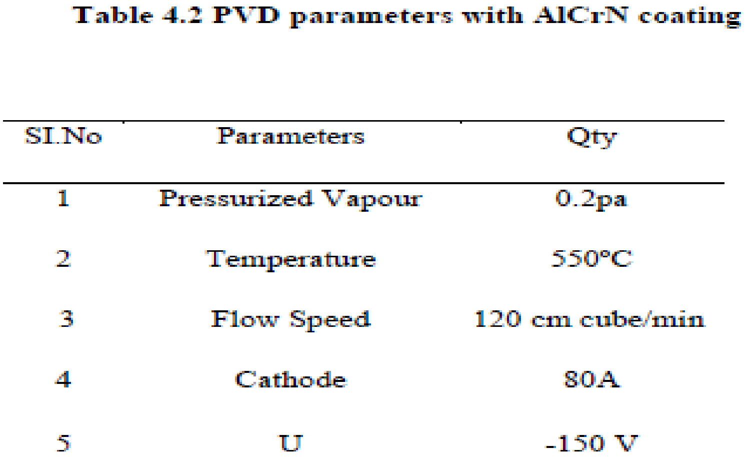

Table 4.2 PVD parameters with AlCrN coating

SI.No	Parameters	Qty
1	Pressurized Vapour	0.2pa
2	Temperature	550°C
3	Flow Speed	120 cm cube/min
4	Cathode	80A
5	U	-150 V

4.2 Microstructural Characterisation Of Materials

The microstructure of feedstock powders and as-deposited coatings was characterized by SEM. Samples from the surfaces of the coatings and from cross sections of the coatings were polished using a series of coarser to finer grades of silicon carbide emery papers and then finally polished with a diamond paste, applied on a velvet cloth that was attached to a rotating disc. In this way, micro-polished surfaces were obtained for further analysis and evaluation. The sample was etched with Nital to reveal microstructure features of interest.

4.3 Scanning Electron Microscopy (SEM)

The external morphology and cross-section of powders were investigated using a Philips FEI XL30 scanning electron microscopy (SEM). A schematic diagram of a typical SEM set-up is shown in Fig. 4.3.

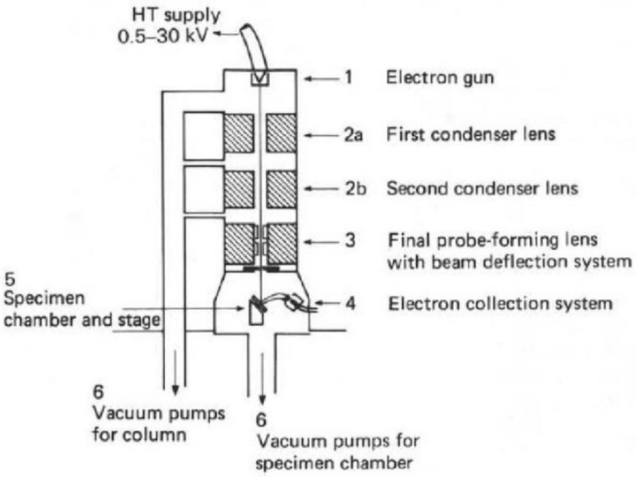

Fig. 4.3 Schematic diagram of the basic components of a SEM

5. RESULT AND DISCUSSION

5.1 Micro-Structural Properties Of The Coating

SEM micrographs of the coating surface showed open pores, unmelted particles and micro-cracks. The BSE image of coating surface (see figure 5.1(b)) shows that the coating thickness is 400µm. The presence of unmelted particles in the spray will induce some porosity in the coating, and this porosity justifies the use of very fine powders, which increases the number of melted particles and decreases the porosity.

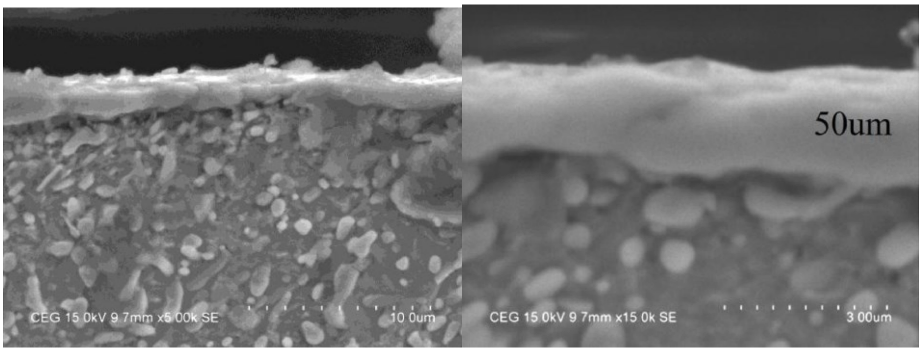

Figure 5.1 Cross-sectional SEM images of a AlCrN coated specimen.

The coatings appear to consist of multiple particle layers (see Figure 5.1(a)), which result from successive impacts of unmelted, semi-molten and molten particles (molten particles being required for the formation of homogeneous coatings).

The coating thickness is found to be 50 microns using Hermit scale through optical microscope. The coated area is found to have the formation of the steel microstructure with intermediate of Ferrite and Austenite with Carbide Particles. Carbide is hard material; as well as in situation like wear, where other metals would wear away but carbide has high quality of resistance.

5.2 Microhardness

Vickers microhardness values of AlCrN coating and substrate are shown in Figure 5.2. Microhardness values that were taken along the cross-section of the sample were decreased regularly. At the same time, the average value of the microhardness of FeCrB top coatings is significantly higher than that of the substrate. However, Cr played a major role in the difference in hardness of FeCrB top coating due to its moderate strengthening effect. In addition to Cr content, some inhomogenieties such as porosity, oxides and unmelted particles cause a change in hardness values of the top coating. As indicated in a research [4], concerning flame sprayed coatings, local variation in hardness results from the variation in particle temperatures and velocity which are inherent in the spray process.

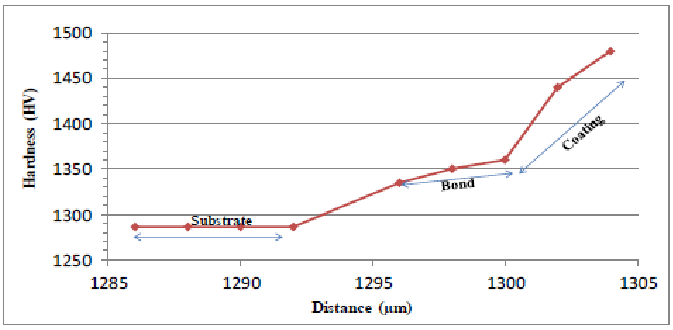

Figure 5.2 Microhardness variation

In the figure 5.2, the Microhardness variation graph shows that average hardness at the surface of the coating reaches maximum as 1400 HV0.1, about three times greater than the substrate hardness which is around 1000-1100 HV0.1 and the hardness value at the interface of coating and substrate shows 1400 HV0.1

5.3 Micro Abrasion Wear Test Analysis

An optical microscopy analysis of the wear craters obtained in this work indicated that in all cases, the abrasive wear mode was grooving abrasion. Figure 5.3 presents an optical microscopy image of a wear crater where only grooving abrasion is visible.

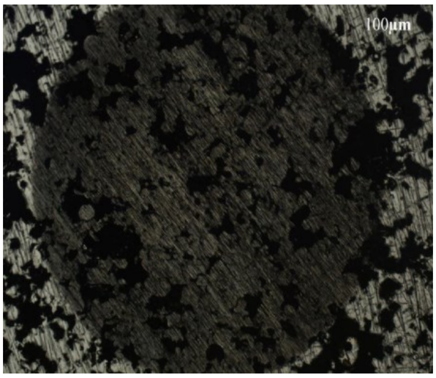

Figure 5.3 Wear craters obtained in experiment (2N, 150rpm)

The results of three-body abrasive tests for the AlCrN coated sample, in terms of the volume loss as a function of testing time and the total wear volume, are shown in Figure 5.3a–c. In Fig. 5.3 a-c the total volume losses of EN 31 steel were tested under the same conditions is included for comparison.

$V = \pi b4/ 64R$ for $b << R$,
V = Wear Volume
b = Wear Crater for 5 and 10 min
R = Radius of bearing balls (25mm)

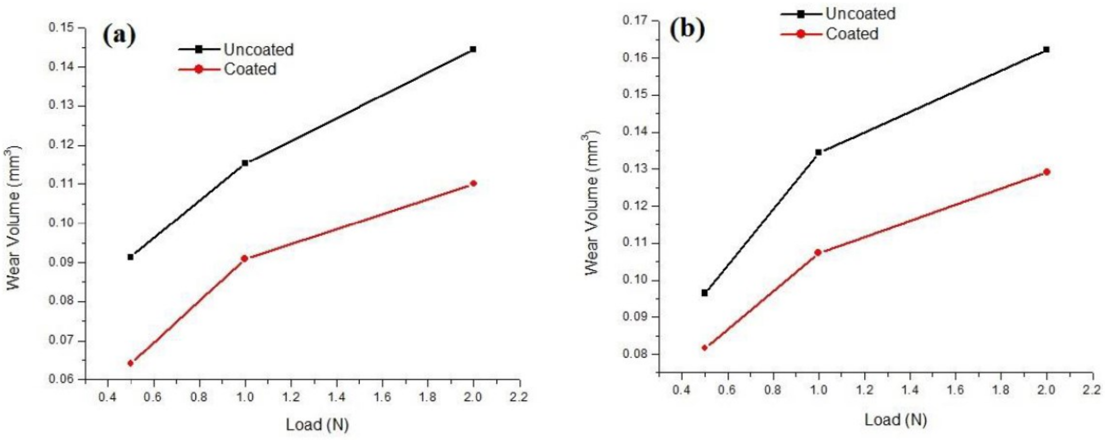

Figure 5.4 Wear volume Vs Load ((a)5minutes, (b) 10minutes

It can be seen in figure 5.4a-c that there is almost a linear relationship between the wear volume and test time (or sliding distance travelled by the rotating ball) for the entire coated sample tested, despite increases in the ball roughness as testing progresses. The volume loss of the High carbon steel sample (1000 HV0.1) is twice higher than the volume loss of AlCrN coated High carbon steel (1400 HV0.1). This confirms that the abrasive wear resistant of coated were highly improved than the uncoated sample.

6. CONCLUSION

PVD process was used to coat AlCrN coating on High carbon steel (AISI 52100). The results showed that the hardness across the coating surface was much higher than uncoated steel substrate. It increased from 1280HV to 1480HV.

The micro-abrasion resistance of AlCrN coated steel substrate was analyzed as a function of applied load and time of contact. Then their results were compared with the uncoated steel. The results show that the wear resistance of coated surface has improved significantly. Hence PVD coating of AlCrN alloy on High carbon steel enhances wear resistance and increases the hardness.

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