ABSTRACT

Surface modification by coatings has become an essential step to improve the surface properties such as wear, corrosion and oxidation. The largest application of Physical Vapor deposition(PVD) coatings is in surface protection for example in metal cutting field-particularly for twist drills, gear cutting tools, forming tools such as in cold backward impact of copper components, polymer processing machinery(injector screws),moulds for plastic, in metrology field thread gauges and slip gauges, in medical applications for surgical tools, in food industries and in automotive parts of racing cars.

Amongst various PVD techniques, Cathode arc evaporation (CAE) is an especially attractive PVD deposition technique both for its unique abilities (high deposition rates, highly ionized vapor which allows ion energy control through substrate bias voltage)and excellent adhesion, hence is widely used in the coating industry.

The fourth-column transition metal mononitrides have interesting properties resulting from their exhibition of both metallic and covalent bonding characteristics. The covalent crystalline properties are: high melting points; extreme hardness and brittleness and excellent thermal and chemical inertness. The metallic characteristics are electrical conductivity and metallic reflectance. Titanium nitrides (TiN) and Zirconium nitride (ZrN) have been the most successful in industrial application as decorative coatings and to Prevent Chip Welding in Cutting tools. First TiN Coating by PVD technique on Cutting Tools took place in 1960. Because of their extreme wear resistance, they are used as hard-coating thin films to expand lifetimes of mechanical compounds such as cutting tools and dies. TiN and ZrN possess the same FCC crystal structure with a lattice misfit of 7.1% that can be easily overcome by misfit dislocations, a shear stiffness difference of about 30Gpa.Compared with conventional metal nitrides, ternary nitrides such as (Ti,Al)N,(Ti,Cr)N and (Ti,Zr)N possess great advantages in micro hardness and oxidation resistance due to their respective alloying effects.

In the present investigation TiN, ZrN and ZrTiN of varyingthickness(1.5μ, 2.0μ,2.5μ,3μ, and 4μ) were deposited on 316 stainless steel by cathode arc evaporation technique at Multi Arc (I) Ltd. Umargoan Micro structural characterization was carried out by using SEM Hitachi 3400 and Jeol 5610, grain size measurement and phases present were determined by X ray diffraction(XRD:PHILIPS PANalytica MRD),Corrosion and Wear

performance was determined by using potentiostat (EG&G PAR 273A and Gamry potentiostate(reference 600)) and Pin on Disc tribometer (Model TR-20, DUCOM-Banglore) respectively.

The SEM observations indicate the presence of macroparticles (typical of cathode arc evaporation technique) in the thin films. The number of macro-particles per square centimeter was significantly higher in the TiN and Ti_xZr_yN than ZrN, probably owing to the lower melting point of the titanium target material.

The XRD results indicate that for Ti-N thin films instead of schiometric TiN, Ti_2N is obtained. Hard coatings like TiN normally contain a high degree of internal (usually compressive in-plane) stress owing to lattice distortion and thermal mismatch effects; it is, therefore, difficult to produce single-layer TiN coatings thicker than 6–7 μm. Lower stresses are present in Ti_2N coatings and can be deposited with thicknesses up to tens of micrometers without encountering adhesion problems on typical substrate materials employed. In addition to Ti_2N,small peak corresponding to $TiN_{0.9}$ is obtained, therefore composition of the coating is not purely Ti_2N,consequently in all the experimental studies and results instead of Ti_2N,Ti-N is considered ZrN thin films have FCC structure. In the case of F.C.C. materials, the preferred texture for low substrate deposition temperatures involves (111) planes (being parallel to the surface) since the (111) planes are the most densely packed planes in F.C.C However at high temperature (200^0 C) or when negative bias is applied, orientation changes from (111) to (200).The coexistence of both ZrN (111) and ZrN (200) contribute to high macro stress within the coating. In the present investigation 2μ ZrN and 2.5μ ZrN, peak intensity of ZrN (111) and ZrN (200) is high indicating high macro stress within the coating. A solid solution of (Ti,Zr)N, with single FCC structure and no evidence of phase separation, was formed for multi component Ti–Zr–N coatings by many researchers (R. L. Boxman etal, E. Etchessaharet al, P. Duwez at al, R. Kieffer et al, O. Knotek et al, L.A. Donohue et al). However in this case we obtained separate phase of ZrN and Ti_2N in ZrTiN thin films.This may be due to formation of Ti_2N instead of TiN which has tetragonal crystal structure different than FCC ZrN structure. Thus the solid solution of ZrN and Ti_2N may not have formed either due to large variation in Lattice parameter and different crystal structure or both, since this does not fulfill the criteria for formation of solid solutions according to Hume Rothery rules.

The corrosion behaviour of the coating-substrate systems can be characterized by current density-potential measurement. Electrochemical experiments proved to be good test for studying the resistance and compactness of coatings. The potentiodynamic (ASTM G59) and Electrochemical impedence spectroscopy ((EIS) (ASTM G610)) was used to characterize the corrosion resistance in various industrial environment like 1N H_2SO_4, (Widely used acidic environment in chemical industries) 3.5%NaCl(Neutral marine environment), 0.1N HCl (used for processsing of polymers) and 11pH Na_2SO_4 (alkaline environment used in paper and pulp industries) was used. In case of Ti-N coating in 1N H_2SO_4 a shift in the lower value of current (i.e. low corrosion rate) is observed. A horizontal peak corresponding to additional phase is also observed. Similar behaviour was observed by ZrN and Zr-Ti-N however the difference is less. In case of Corrosive environment containing chlorides (3.5%NaCl & 0.1N HCl) pitting corrosion is observed, as depicted by little change of current with potential for some potential range where the passive layer protects specimen surface from dissolving. In this region, anodic current density increases dramatically with potential due to a pitting corrosion mechanism initiated at the local defects of the film also in addition to this cathodic polarization at the coated samples starts at a current lower than the stainless steel, but near the corrosion potential the coated sample current increases until it becomes almost equal to that of stainless steel. 11pH Na_2SO_4 is a very mild corrosive environment, hence the value of corrosive current observed is very low and uniform corrosion is observed. In case of EIS results at high frequency (capacitive nature) difference in impedence value for thickness of different coating was less, however at low frequency (resistive nature) difference observed was more, this may due to more time for interaction of the ac current at the discontinuity. Similar behaviour was observed in ZrN and Zr-Ti-N thin films but extent of protection is varying. The extent of the corrosion attack is depicted in terms of SEM and EDX analysis after potentiodynamic test.

Most pin on disc machines are used for measuring sliding wear and friction properties, but severe adhesive wear or galling is studied as well. For present investigation, pin on disc, the coating was applied to the flat end of pin and steel disc made of EN24 of hardness Rc 55 was used as counter face. The test is very versatile since testing conditions can be greatly varied. The results were presented in terms of variation in COF with time. In addition to this, SEM and EDX analysis at various points, line and area at different magnification was taken. The aim was to determine the type of failure occurring (adhesive, abrasive or tribochemical) and an attempt was made to determine the composition of the debris. The results indicate that oxidation of TiN to TiO_2 might have occurred; however in absence of sophisticated instrumentation available the composition cannot be determined with confidence.

The thesis is divided in six different chapters, chapter 1 consisting of introduction and importance of present research, second chapter corresponds to the literature survey about the properties of coatings already available, third chapter involves detailed mechanism of wear and corrosion.. Fourth chapter gives information about instrument, experimental details and procedure. Fifth chapter is results and discussion of the deposited coatings and their correlation with the literature available. Finally in sixth chapter the peculiar behaviour of the coating is depicted in terms of monograms as conclusions. Further summary and scope of extending present work has been proposed.