SUMMARY

Preparation and Characterisation of Zirconium based Thin Films for Functional Applications

Surface modification by coatings has become an essential step to improve the surface properties such as wear, corrosion and oxidation. Various conventional techniques are utilized for depositing the desired material on to the substrate to achieve surface modification. The development of 'clean' technologies in all spheres of industrial manufacturing is today an essential task required and initiated by environmental laws and programmes of countries around the world has lead into the progress of vacuum based technology like Physical Vapor deposition(PVD) and chemical and plasma-assisted chemical vapour deposition (CVD, PACVD) and thermal spraying

Cathodic 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, excellent adhesion), and it is widely used in the coating industry. It is well known that composition, structure and properties of the deposited films depend on the process parameters such as growth temperature, substrate bias voltage and gas pressure in the vacuum chamber. Vacuum arc evaporation has mainly performed as continuous target/cathode evaporation using permanently burning arcs. The random movement of the cathode spots of such more or less freely burning arcs is the main reason for most of its disadvantages. Instabilities of the discharge, unequal erosion of the cathode surface, random overheating and consequently local melting of the normally cold surface result from the random motion of the spot. Therefore droplets are ejected from the cathode spot that may damage the growing film. Consequently, it will be useful to control the spot motion to minimize the droplet emission.

Among the transition metal compounds, TiN sits in a preferential position with suitable average properties meeting most requirements for wear and corrosion-resistant coatings. It is reasonably hard, pleasant in aspect and cheap. TiN is known as the most universal coating and shares about the 90% of coating market .TiN is the primary coating in present use. Zirconium nitride(ZrN) exhibit very interesting properties such as high hardness, high melting point, high corrosion resistance. Their optical and mechanical properties intensively depend on the nitrogen composition. The stoichiometric nitride

ZrN is metallic-like with a gold, yellow color; it is the thermodynamically stable phase, stable upto 600^0C

TiN had a very low oxidation resistance, a drawback that made it less suitable for applications where the service temperature could reach several hundreds of degrees Celsius, as it is the case in the tip of cutting tools working at very high cutting speed. In order to meet the specific needs of applications especially in the field of tribology,

further development of conventional hard thin films lies in depositing compounds with a complex structure, *i.e.* ternary or quaternary mixed phases. By incorporating additional metals (aluminum, chromium, niobium vanadium or zirconium) or metalloids (carbon, boron or oxygen), coatings consisting of ternary or quaternary mixed phases with improved properties. Both Al and Zr could increase the temperature for initiating oxidation of the coatings by more than 200°C, in comparison to TiN .

The corrosion process is determined by the ion release of metallic species and is therefore mainly surface phenomena. Wear like corrosion is one of the most important failure modes of vast majority of mechanical components and is a surface property that can be minimized by altering the surface chemistry and microstructures.

In applications such as chemical apparatus processing and the food industry, however, the mechanical loads occurring are superimposed by corrosive attack. Requirements for coatings withstanding this complex load include chemical inertness in the media concerned, but also microstructure demands such as a smooth surface, dense morphology without micro porosities and diffusion pathways, a homogeneous stoichiometry and a good adhesion between the coating and the substrate material

The deposition parameters (substrate temperature, plasma characteristics, etching time, substrate bias, etc.) together with the *substrate characteristics* (e.g. composition, microstructure, topography) determine the *coating characteristics* (thickness, chemical composition, microstructure and topography, etc.). The factors affecting both wear and corrosion resistance of thin films include substrate composition (determines morphology of coating),adhesion (low adhesion results in delamination of coating due to H_2 evolution during corrosion test and failure during wear),porosity in the coating results in galvanic effect observed at substrate coating interface in addition to this wear resistance also decreases. Similar to corrosion wear resistance is improved by using multiconstituent (increase in densification & overall hardness) and multilayered(inhibition to crack propogation (wear) and porosity(corrosion)) coatings.

In the present investigation thin films of TiN, ZrN and ZrTiN of varying thickness were prepared by Cathode arc evaporation PVD technique at NBD(New business development centre) of Multiarc (I) ltd. Umargoan were used. Film thickness was chosen as the controlling parameter, and single-variable experiments were conducted. The resulting coatings were characterized using the following techniques: Scanning Electron microscope (Hitachi 3400 and Joel 5610) Cu Kα X-ray diffraction analysis (Philips PANANALYTIC Xpert pro diffractometer), potentiodynamic test for corrosion resistance (EG & G PARC 273 & Gamry potentiostate(reference 600)) and results were obtained in terms of E Vs log I and Impedance Vs frequency/Impedence vs Phase ang, Pin on disc (Windocom Model TR-20,DUCOM-Banglore) results were obtained in terms of variation in COF vs Time for Wear resistance measurement. The surface morphological and chemical changes before and after corrosion and wear were measured in terms of SEM and EDX analysis.

For complete characterisation various instruments like SEM and XRD is used. SEM has high depth of focus of electron beam permitting detailed imaging of rough surface over wide range of magnification,5X-50,000X.SEM analysis indicates that the number of macro-particles per square centimeter was significantly higher in the TiN and TixZryN than ZrN, probably owing to the lower melting point of the titanium target material.

X-ray diffraction (XRD) is used as a non-destructive analysis method for phase determination.

In the present investigation 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, 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.This may be due to formation of Ti_2N instead of TiN which has tetragonal crystal structure different than FCC ZrN structure 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. In the present investigation, the potentiodynamic (ASTM G59) was used to characterize the corrosion resistance in various industrial environment like 1N H_2SO_4 , (Widely used acidic enviornment 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 ZrTi-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 $Na_2SO_4$was 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.

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 testing coatings, the coating is applied to the end of flat ended or hemispherical pin or to the disc or to both. The test is very versatile since testing conditions can be greatly varied. TR-20,DUCOM-Banglore.The results were presented in terms of variation in COF with time. In addition to this, SEM and EDX analysis at various point, 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 indicates that oxidation of TiN to TiO_2 might have occurred, however in absence of sophisticated instrumentation available the composition cannot be determined with confidence.