PREFACE

Tribology, the science and technology of interacting surfaces in relative motion and encompassing the phenomena of friction, wear and lubrication, has progressed well since the coining of this term in 1966. The technological importance of the field can be gauged by the fact that most of the time the failure of machines is not by the breakage of the component but by wear of machine elements which renders them unsuitable to perform their intended function and generates a need for their replacement. Wear, the progressive loss of material from the surface of bodies in relative motion, is the major cause of material wastage and loss of mechanical performance and any reduction in wear can result in considerable savings. Friction is a primary cause of wear and energy dissipation. Considerable savings are expected to be made by improved friction control. It is estimated that one third of the world's energy resources in present use is needed to overcome friction in one form or another. Lubrication is an effective way of controlling wear and reducing friction.

Lubrication at elevated temperature is a serious problem in a large number of applications such as power generation, transport, materials processing, and high temperature bearing etc. especially those that include temperatures above 350 °C since liquid lubricants degrade rapidly under these conditions. Keeping in view the requirements of the high technology areas the use of solid lubricants (SLs) is the only viable alternative to reduce friction in many harsh environments. Solid lubricants are used when liquid lubricants do not meet the advanced requirements. The most widely used SLs in industry are graphite, boron nitride, and MoS_2 because of their easy-shearing lamellar structure that results in low coefficient of friction. Other SLs include noble metals (Au, Ag, Pt, and Cu), inorganic fluorides (LiF, CaF_2, and BaF_2), and a few metal oxides (NiO, PbO, B_2O_3, and MoO_3). However, there is no single solid lubricant that displays a low coefficient of friction in a broad range of environmental conditions. To remediate the shortcomings of the monolithic SL approach, solid lubricating coatings containing a combination of solid lubricants have been developed which are primarily used to control friction and wear under severe application conditions such as high vacuum, aerospace, high-speeds, high loads, and very low or high temperatures.

In the present study, Ni-Al based solid lubricating coating, namely, Ni-Al-Ag-MoS_2 (designated as NAMB0), Ni-Al-Ag-MoS_2-5 wt. % hBN (NAMB5) and Ni-Al-Ag-MoS_2-10 wt. % hBN (NAMB10), containing a combination of solid lubricants Ag, MoS_2 and hBN have been deposited by atmospheric plasma spray technique on Inconel 718 substrate. The amount of Ag and MoS_2 has been kept fixed at a level of 10 wt. % each whereas content of hBN has been added as 5 wt. % and 10 wt. % to analyze the effect of hBN addition on hardness. The tribological behavior of the coatings has been evaluated by carrying out sliding wear tests against alumina ball under different loads (5, 10, 15, 20 N) and sliding speeds (0.3, 0.5, 0.7, 0.9 m/s) at temperatures ranging from room temperature (RT) to 800 °C using a pin on disk tribometer. The primary focus of the study is to understand the elevated temperature tribological behavior of atmospheric plasma spray deposited Ni-Al based coatings containing a combination of low temperature and high temperature solid lubricants. The study also aims to explore the possibility of a synergistic action among Ag, MoS_2, and hBN (which is a clean lubricant and stable at high temperatures) lubricants in extending the regime of effective lubrication of such coatings from RT to 800 °C.

The thesis has been organized in the following five chapters:

Chapter-1 contains the introductory remarks highlighting the technological importance of the problem under investigation.

Chapter-2 begins with a brief descriptions of phenomenon of wear, its different types, factors that affect wear and lubrication (both liquid and solid). It is followed by a note on the necessity of solid lubrication including a brief description of different solid lubricants. An extensive survey on various techniques used for deposition of wear resistant coatings with special emphasis on the importance of thermal spraying process, the requirements for the plasma spraying and key process parameters which affect the microstructure and the quality of coatings is also included in the chapter. The chapter also contains a brief elucidation of high temperature wear of materials. A comprehensive review of literature pertaining to elevated temperature tribological behavior of the composites and coatings containing solid lubricants coatings also forms a part of the chapter. The formulation of the problem is presented at the end of chapter.

Chapter-3 outlines the details of experimental procedures followed in the current investigation. In the present study, nickel powder (Cu; 99% purity; particle size- (80-120) µm), aluminum powder (Al; 99% purity; particle size- (20-50) µm), MoS_2 powder (purity- 99 %; particle size- (30-70 µm), Ag powder (purity- 99 %; particle size- (45-75) µm), and hBN (purity- 99 %; particle size- 70 nm) have been used to prepare the composite powder through ball milling for the coatings to be deposited through atmospheric plasma spray route. Ar and H_2 have been used as primary and secondary gases, respectively, during the plasma spray deposition. Three coatings, namely, Ni-Al-Ag-MoS_2 (designated as NAMB0), Ni-Al-Ag-MoS_2-5 wt. % hBN (NAMB5) and Ni-Al-Ag-MoS_2-10 wt. % hBN (NAMB10), have been deposited by 3 MBM plasma gun (Anod

Plasma Spray Limited, Kanpur, India) on Inconel 718 substrate. X-ray diffractometry and high resolution-scanning electron microscope (HR-SEM) equipped with energy dispersive spectroscopy have been used to characterize the coatings. The detailed procedures followed in regard to measurement of porosity using image J analyzer software and hardness have been presented in the chapter. The details of the procedure used for tribo-testing of coatings along with various parameters are also included in the chapter. All the tests have been performed using 'a rotary ball on disk configuration' against a counterface of alumina ball at different loads (5, 10, 15, 20 N), speeds (0.3, 0.5, 0.7, 0.9 m/s) and different temperatures (RT, 200,400, 600 and 800 °C) according to ASTM G99-05. The chapter also provides the details of techniques used for analysis of worn surfaces of all the coatings and alumina ball.

Chapter-4 describes results on the structure and property characterization of Ni-Al-Ag-MoS_2 (NAMB0), Ni-Al-Ag-MoS_2-5 wt. % hBN (NAMB5), and Ni-Al-Ag-MoS_2-10 wt. % hBN (NAMB10), coatings deposited through plasma spray process. XRD patterns of composite coatings reveal the presence of Ni based solid solution (γ phase), Ni_3Al phase (γ′ phase) and NiAl phase and the peaks corresponding to solid lubricants indicating that powders are deposited without any oxidation or disintegration. All the coatings exhibit a fairly compact and dense structure comprising of the droplets impacted on the substrate, however, the coatings containing hBN i.e., NAMB5 and NAMB10, have been observed to be relatively less dense in comparison to NAMB0, containing no hBN. The measured thickness is about 250 µm for all the composite coatings. The area percent porosity has been found to increase with increasing addition of hBN in the coatings and the corresponding porosities for NAMB0, NAMB5, NAMB10 are observed to be 4.8 ± 0.7%, 8.0 ± 1.0% and 24 ±1.4%, respectively. The hardness of coatings as measured by a Vickers hardness tester are 182.4, 164.6, and 155.3 $HV_{0.2}$, for NAMB0, NAMB5 and

NAMB10, respectively. The hardness of the coatings has been found to decrease with addition of hBN. The increase in porosity and decrease in hardness has been attributed to the poor wettability and sinterability of hBN which hampers the close contact between other constituent materials of coating and hence, the densification process.

The chapter also contains the results and discussion pertaining to the friction and wear characteristics of NAMB0, NAMB5 and NAMB10 coatings. The results on tribological behavior are presented in three parts: (i) the room temperature (RT) behavior of coatings under different loads and a constant sliding speed, (ii) elevated temperature tribological behavior at a constant load and speed and (iii) high temperature tribological behavior at different speeds and temperatures but under a constant load.

The room temperature friction and wear behavior has been examined by carrying out the tests at different loads of 5, 10, 15 and 20 N but at a constant sliding speed of 0.5 m/s for a total sliding distance of 500 m. The friction coefficient has shown a fluctuating trend of variation with distance, typical of a pin-on disk geometry, at all the loads but with a varying degree of amplitude of fluctuations. However, the coating containing 5 wt. % hBN (NAMB5) has shown a relatively lower coefficient of friction (COF) with relatively smaller amplitude of fluctuations in comparison to both NAMB0 and NAMB10 under all the loads used in the study. The average COF has been observed to decrease with increasing load from 5 to 15 N followed by a slight increase till 20 N for all the coatings. The coatings NAMB5 and NAMB10 containing hBN have shown a consistently lower COF in comparison to Ni-Al–Ag–MoS_2 (NAMB0) coating at all the loads. However, the coating with 5 wt. % hBN has shown the lowest COF at all the loads in the present investigation and a minimum COF value of 0.29 achieved at a load of 15 N.

The wear rate for all the coatings has been observed to decrease with increasing load from 5 to 15 N followed by an increase beyond 15N. NAMB0 coating has shown a consistently higher wear rate than other composite coatings at all loads. It has further been observed that the wear rate of the composite coating gets significantly reduced with the addition of hBN indicating thus, the occurrence of a probable synergetic action between the solid lubricants. However, the lowest rate of wear has been observed for NAMB5. The worn surface of the coated specimens and the counterpart ball under different loads have been examined under FESEM equipped with EDS to explore the operative mechanisms of wear. SEM micrographs of worn surface of the composite coatings NAMB0, NAMB5 and NAMB10 revealed the presence of small wear debris, scoring marks along the direction of sliding, some pits and a continuous or discontinuous layer of transferred material with varying degree of compaction, smoothness and extent of coverage of the area of worn surface depending on the conditions of load. The worn surfaces have been subjected to X-ray diffraction and Raman spectroscopy to explore the formation of new phases on the sliding surface due to chemical reactions during sliding process. X ray analysis has not revealed any peaks corresponding to any new phases except those of lubricants. However, Raman spectrum corresponding to NAMB0 coating has shown the presence of Ag_2MoO_4 only at a load of 15 N whereas peaks of Ag_2MoO_4, MoO_3, AgO and $NiMoO_4$ phases along with that of hBN have been observed for NAMB5 and NAMB10 coatings. The observed behavior has been explained on the basis of the formation and extent of compaction of the transfer layer containing solid lubricant on the sliding surface, the transfer of solid lubricant/s from coating to the alumina ball and the generation and presence of new lubricating phases due to tribo-chemical reactions at the interface caused by the temperature rise.

Under the conditions used in the present investigation, the mechanism of wear in NAMB0 coating appears to be a mixture of ploughing and delamination at a load of 5 N and 10 N whereas at relatively higher loads of 15 and 20 N the abrasive wear mechanism is dominating. As far as coating containing 5 wt. % hBN is concerned the operative mechanisms are adhesion and transfer layer formation under all the loads. The mechanism of wear for coating having 10 wt. % hBN is adhesive in nature at loads of 5, 10 and 15 N whereas a mix of adhesion and delamination at the highest load of 20 N used in the current study.

In order to examine the performance of coatings at elevated temperatures, the friction and wear behavior has also been evaluated at RT, 200, 400, 600 and 800 °C but at a fixed normal load of 5 N and sliding speed of 0.3 m/s by conducting tests against alumina ball. The variation of friction coefficient with time for the composite coatings at RT, 200, 400, 600 and 800 °C has shown a fluctuating trend with varying relatively larger amplitude for all the coatings from RT to 400 °C. However, the amplitude of fluctuations has been found to reduce at the highest temperature of 800 °C for all the coatings. At 800 °C, the coatings containing hBN have shown a relatively smoother variation in comparison to the one without hBN. Also, the coating containing 5 wt. % hBN i.e., NAMB5 has been observed to maintain a lower coefficient of friction of around 0.2 during the entire test. The average COF for NAMB0 coating has been found to decrease from RT to 200 °C followed by an increase at 400 °C before decreasing again to a low value of 0.28 at 800 °C. The friction coefficient of coatings containing hBN is found to decrease continuously with increase of temperature from RT to 800 °C. However, NAMB5 coating has shown the lowest coefficient of friction at all the temperatures used in the study and the COF is observed to reach a value as low as 0.23. The wear rate of NAMB0 composite coating is found to first decrease with increasing temperature from RT to 200 °C and increase thereafter as the temperature is raised to 400 °C beyond which the wear rate decreases again till 800 °C. The wear rate has been observed to decrease continuously with increasing temperature from RT to 800 °C for the coatings containing hBN, namely, NAMB5 and NAMB10. However, NAMB5 has shown the lowest rate of wear among all the coatings at all the temperatures used in the study. The decrease in wear rate for NAMB0 coating from RT to 200 °C has been attributed to the lubrication provided by MoS_2 whereas an increase in wear rate of NAMB0 coating from 200 to 400 °C has been ascribed to the loss of lubricating potential of MoS_2. However, a decrease in wear rate beyond 400 °C has been credited to the formation of silver molybdates and other high temperature lubricants along with the presence of glaze. The decreasing rate of wear for NAMB5 and NAMB10 coatings has been attributed to the formation of Ni and Mo oxides, silver molybdates, the transfer of hBN to the counterface and the synergetic action of hBN in conjunction with Ag, MoS_2 at temperatures from RT to 400 °C and lubricious molybdates at temperatures beyond 600 °C.

The chapter further describes the results and discussion on the tribological behavior of NAMB0, NAMB5 and NAMB10 coatings slid under different speeds (0.3, 0.5, 0.7 and 0.9 m/s) and temperatures (RT, 200, 400, 600, 800 °C) at a constant load of 5 N. Both the coefficient of friction and the wear rate have been found to decrease with increasing speed from 0.3 to 0.7 m/s with a marginal increase beyond that for all the coatings. However, coating NAMB5 has been found to exhibit better lubricity in comparison to other coatings at all the sliding speeds and temperatures and coefficient of friction for this coating has been found to decrease from 0.51 to 0.23 at a sliding speed of 0.3 m/s and from 0.48 to 0.1 at a sliding speed of 0.7 m/s with the increase in temperature from RT to 800 °C. The results indicate the existence of a synergistic action of hBN in combination with Ag and MoS_2 in providing lower friction and wear highlighting thus, the potential of hBN as an effective lubricant in stabilizing the friction in a wide range of speeds and temperatures. The observed behavior has been attributed to the presence of transfer layer containing lubricants, its extent of coverage and degree of compaction, transfer of coating material (including hBN) to counterface of alumina, lubricious phases formed owing to the tribo-chemical reactions and a synergetic action of hBN with Ag and MoS_2, as explained earlier.

At elevated temperatures, the mechanism of wear in NAMB0 coating appears to be a mixture of ploughing, abrasion, adhesion, delamination and glaze formation depending upon the combination of speed and temperature. For NAMB5 coating, operative mechanisms are a mix of adhesion and abrasion depending on the sliding speeds from 0.3 to 0.9 m/s, from RT-400 °C and glaze layer (tribo-layers) formation & adhesion at elevated temperatures at all the sliding speeds. The dominating mechanisms of wear for NAMB10 coating are tribo-oxidation and adhesion from 200 to 800 °C.

Chapter-5 presents the major conclusions of the present study pertaining to microstructure and properties of deposited coatings along with their friction and wear characteristics under different loads, speeds and temperatures and the role of hBN in extending the regime of effective lubrication.