Preface

Tribology is a multidisciplinary science and engineering field that examines and comprehends the intricate interactions between surfaces in relative motion. It encompasses the study of friction, wear, lubrication, and the overall behaviour of materials in contact with one another, playing a pivotal role in the functioning and longevity of mechanical systems, from the everyday machines we use to the sophisticated industrial equipment that drives our modern world. Tribology's significance lies in its ability to enhance machinery efficiency, reduce energy consumption, and prevent premature wear and failure, ultimately impacting a wide range of industries and our daily lives. Wear refers to the progressive loss of material from solid surfaces in contact, which is the major cause of material wastage and loss of mechanical performance, and any reduction in wear can result in considerable savings. Friction serves as the main cause of wear and energy dissipation, with estimates suggesting that about one-third to half of the world's energy is consumed due to friction. A significant portion of global resources are expended in efforts to overcome friction in various ways. The use of lubrication, whether in liquid or solid form, proves to be a highly effective method for managing wear and friction.

Lubrication at elevated temperatures is a critical aspect in numerous industrial sectors, such as aerospace, automotive, manufacturing, and military industries. At high temperatures, gas lubrication technology has not matured. Liquid lubricant is restricted to temperatures below 350 °C due to decomposition and rapid degradation at elevated temperatures. Certain solid lubricants have the capability to withstand temperatures as high as 1000 °C. The utilization of high-temperature solid lubricants presents itself as the sole feasible alternative for friction reduction in numerous high-temperature applications, particularly those surpassing 350 °C. The most widely used solid lubricants in the industry are soft metals (Cu, Au, Ag, etc.), layered materials (*h*BN, MoS_2, WS_2, graphite, etc.), metal oxides (CuO, NiO, MoO_3, etc.), double oxide phases (Ag_2MoO_4, $Ag_2Mo_2O_7$ etc.), alkaline halides (BaF_2, CaF_2, etc.), as well as MAX phases (Ti_3SiC_2, Ti_2AlC, etc.). It is important to have a low coefficient of friction, strong resistance to wear and oxidation qualities for use in a variety of industrial applications. Due to the impracticality of achieving the aforementioned properties using bulk monolithic materials, much emphasis has been placed on the advancement of solid lubricating wear-resistant composites containing a combination of solid lubricants as a potential remedy for these shortcomings.

Ni_3Al-based intermetallic compounds possess excellent properties at elevated temperatures, such as high-temperature strength, hardness, high melting point, chemical inertness, and excellent oxidation, as well as corrosion resistance, which make them suitable for various industrial applications like gas turbine engine parts, aerospace, tooling and machining, rolling and forming tools, defence industries, internal combustion engines and various furnace components**.** However, the friction and wear characteristics of Ni_3Al intermetallic compounds have been constrained by their inherent brittleness at ambient and elevated temperatures. It has been indicated that the friction and wear performance of Ni_3Al intermetallic compounds can be improved by integrating alloying elements, other reinforced phases, solid lubricants and regulating the reaction sintering process.

In view of the above, Ni_3Al-based composites containing solid lubricants (Ag, WS_2, Cu-modified *h*BN nanosheets (Cu-*h*BN) either singly or in combination, i.e., Ag-WS_2, Ag-Cu-*h*BN and WS_2-Cu-*h*BN) have been fabricated by vacuum hot press sintering. The tribological performance of sintered composites has been evaluated at room temperature (RT), 200 °C, 400 °C, 600 °C and 800 °C by carrying out dry sliding wear tests at a constant load of 10 N and sliding speed of 0.2 m/s using a high-temperature ball-on-disk tribometer against silicon nitride (Si_3N_4) ball as counterpart. The primary aim of the study is to examine the possibility of occurrence of synergistic action between a combination of solid lubricants, i.e., Ag-WS_2, Ag-Cu-*h*BN and WS_2-Cu-*h*BN in realizing low friction and wear over the entire range of temperature from RT to 800 °C. The study has been divided into three parts based on the addition of solid lubricants: (i) Synthesis and high-temperature tribological behaviour of the Ni_3Al, Ni_3Al-10wt.% Ag, Ni_3Al-10wt.% WS_2 and Ni_3Al-5wt.% Ag-5wt.% WS_2 composites, (ii) fabrication and elevated temperature tribological characteristics of Ni_3Al, Ni_3Al-10wt.% Ag, Ni_3Al-10wt.% Cu-*h*BN, and Ni_3Al-5wt.% Ag-5wt.% Cu-*h*BN composites, and (iii) Elevated temperature tribological characteristics of Ni_3Al, Ni_3Al-10wt.% WS_2, Ni_3Al-10wt.% Cu-*h*BN, and Ni_3Al-5wt.% WS_2-5wt.% Cu-*h*BN composites.

The thesis has been structured into the following six chapters.

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

Chapter 2 starts with a brief description on composites and their types, followed by a detailed survey on the processing routes to develop metal-based composites with special emphasis on the vacuum hot press sintering technique. The chapter also provides a brief overview of the concept of wear, its types and the factors that influence wear and lubrication (solid and liquid). It further highlights the necessity of solid lubrication including a brief description of different types of solid lubricants. The chapter also delves in the architecture of high-temperature solid-lubricating materials. This is followed by an exhaustive review of literature on the tribological behaviour of Ni-based and intermetallic (Ni_3Al and NiAl) based high temperature solid lubricating composites or coatings with special emphasis on Nickel Aluminide (Ni_3Al) matrix composites containing hard phases, 2D materials and other solid lubricant and also sheds light on the operative mechanisms of wear prevailing in the dry sliding of such composites from RT to 800 °C. The chapter ends with the formulation of the problem and the major objectives of the study.

Chapter 3 outlines the details of materials and the experimental procedures undertaken for the synthesis and characterization of Ni_3Al intermetallic compound, Cu- modified *h*BN nanosheets (Cu-*h*BN) and Ni_3Al-based composites. In current investigation base Ni_3Al and its composites containing a single solid lubricant (Ag, WS_2, Cu-*h*BN) and a combination of solid lubricants (Ag-WS_2, Ag-Cu-*h*BN and WS_2-Cu-*h*BN) have been synthesized by vacuum hot press sintering. The X-ray diffraction analysis has been employed to confirm the phases, whereas distribution of the phases has been analysed using Field Emission Scanning Electron Microscopy (FE-SEM) and Energy Dispersive X-ray analysis (EDX) and elemental mapping. The density and hardness of composites have been measured by using the Archimedes principle and Vickers hardness tester. The friction and wear characteristics have been examined by carrying out dry sliding tribo-tests using a unidirectional ball-on-disc rotary tribometer (DUCOM, India) with a Si_3N_4 ball (ϕ: 6mm, Vickers hardness: 16.2 GPa) as a stationary counterpart at different temperatures (RT, 200 °C, 400 °C, 600 °C and 800 °C) and a constant normal load of 10 N with a sliding speed of 0.2 m/s, following the ASTM G99-95 standard test method. The test duration was kept 30 minutes corresponding to a total sliding distance of 360 m. The worn surfaces of the composites as well as the counterface balls have been examined under the FESEM, whereas the tribo-chemical analysis of the worn track is done by EDX-Elemental mapping, X-ray diffraction and Raman spectroscopy to reveal the presence of different species and explore the wear mechanisms.

Chapter 4 describes the results and discussion on the characterization and tribological behaviour of Ni_3Al, Ni_3Al-10wt.% Ag, Ni_3Al-10wt.% WS_2, Ni_3Al-5wt.% Ag-5wt.% WS_2 composite specimens at RT, 200 °C, 400 °C, 600 °C and 800 °C. XRD analysis of Ni_3Al-based composites has demonstrated the presence of intense peaks corresponding to Ni_3Al apart from the peaks of Ag and WS_2 confirming that the powders have been sintered under a vacuum environment without any oxidation or disintegration. All the composites have been observed to exhibit a fairly compact and dense microstructure with a uniform distribution of all its constituent elements. The hardness of Ni_3Al gets reduced from 355 ± 5 $HV_{0.2}$ to 313 ± 6 $HV_{0.2}$ by the addition of Ag due to the inherent soft nature of silver, whereas the addition of WS_2 brings about an increase in the hardness of Ni_3Al composite from 355 ± 5 $HV_{0.2}$ to 365 ± 5 $HV_{0.2}$ in Ni_3Al-10WS_2 due to its high hardness. However, the addition of both Ag and WS_2 to Ni_3Al results in a hardness of 345 ± 8 $HV_{0.2}$.

Ni_3Al and the composites Ni_3Al-10wt.% Ag, Ni_3Al-10wt.% WS_2, Ni_3Al-5wt.% Ag-5wt.% WS_2 exhibit a fluctuating trend of variation of coefficient of friction (CoF) at all temperatures. At RT, the coefficient of friction for Ni_3Al appears to stabilize after 200 s and remains constant thereafter till the completion of the test, whereas for the Ni_3Al-10Ag, Ni_3Al-10WS_2, and Ni_3Al-5Ag-5WS_2 stabilization occurs after an initial run-in duration of 900 s, 300 s, and 1000 s, respectively, with relatively less amplitude of fluctuations. At 200 °C, the coefficient of friction for Ni_3Al stabilises after 1300 s whereas for the Ni_3Al-10Ag, Ni_3Al-10WS_2, and Ni_3Al-5Ag-5WS_2 stabilisation takes place after an initial run-in duration of 1000 s, 800 s and 600 s. Apparently, no run-in period could be observed for Ni_3Al at 400 °C while the CoF stabilised after 200 s for Ni_3Al-10Ag, Ni_3Al-10WS_2, and Ni_3Al-5Ag-5WS_2. The Ni_3Al-10Ag composite has shown a relatively large amplitude of fluctuations at 400 °C throughout the period of sliding. At 600 °C and 800 °C, Ni_3Al-10Ag, Ni_3Al-10WS_2, and Ni_3Al-5Ag-5WS_2 have shown an almost steady coefficient of friction for the complete duration of sliding, while the coefficient of friction for Ni_3Al has been found to stabilize after about 200 s of sliding. Ni_3Al, Ni_3Al-10Ag and Ni_3Al-10WS_2 have shown relatively large fluctuations in amplitude in comparison to Ni_3Al-5Ag-5WS_2 composite.

The average coefficient of friction of Ni_3Al decreased from 0.655 to 0.423, and from 0.453 to 0.259 for Ni_3Al-10Ag composite, whereas the coefficient of friction of Ni_3Al-

10WS_2 reduced from 0.421 to 0.239 and that of Ni_3Al-5Ag-5WS_2 diminished from 0.389 to 0.206 as the temperature is raised from RT to 800 °C. A decrease in coefficient of friction for Ni_3Al-5Ag-5WS_2 with increasing temperature has been attributed to the occurrence of a synergistic action of Ag and WS_2 and the formation of lubricous silver molybdates (Ag_2MoO_4 and $Ag_2Mo_2O_7$), MoO_3, WO_3, NiO and $NiMoO_4$ at 600 °C and 800 °C as revealed by FESEM-EDS, XRD and Raman analyses.

The wear rate of Ni_3Al, Ni_3Al-10Ag, and Ni_3Al-10WS_2 has been observed to increase from 3.52 to 5.95 x 10^{-5} mm^3/Nm, 2.96 to 6.66 x 10^{-5} mm^3/Nm, and 1.582 to 2.52 x 10^{-5} mm^3/Nm, respectively, as the temperature is raised from RT to 400 °C followed by a decrease to 2.46 x 10^{-5} mm^3/Nm, 2.3 x 10^{-5} mm^3/Nm and 1.06 x 10^{-5} mm^3/Nm at 800 °C. However, the wear rate of Ni_3Al-5Ag-5WS_2 composite has been observed to decrease continuously from 1.53 x 10^{-5} mm^3/Nm to 0.778 x 10^{-5} mm^3/Nm with increasing temperature from RT to 800 °C. Among Ni_3Al, Ni_3Al-10Ag, Ni_3Al-10WS_2 and Ni_3Al-5Ag-5WS_2, the Ni_3Al-5Ag-5WS_2 composite has shown the lowest coefficient of friction (0.39-0.207) and wear rate (1.53-0.778 × 10^{-5} mm^3/Nm) among all the composites at all test temperatures (RT to 800 °C) due to synergetic effect of Ag and WS_2 over a wide temperature range. The improved tribological performance has been attributed to the formation and presence of NiO, MoO_3, $NiMoO_4$, silver molybdates, and WO_3 over the worn surface of composites and the counterface ball. At low temperatures, Ag and WS_2 operate as effective lubricants, whereas the formation of NiO, WO_3, $NiMoO_4$, Ag_2MoO_4, and $Ag_2Mo_2O_7$ at high temperatures by tribo-chemical reactions contribute to lowering the coefficient of friction as well as wear rate.

The wear mechanism for base Ni_3Al is abrasive and adhesive at RT and 200 °C, which changes to adhesion and delamination at 400 °C, and adhesion and oxidation at 600 °C and 800 °C. The wear mechanism for Ni_3Al-10Ag composite is abrasive and ploughing at RT, and abrasive and adhesive at 200 °C, which changes to adhesion and ploughing at 400 °C, and adhesion and oxidation at 600 °C and 800 °C. The wear mechanism for Ni_3Al-10WS_2 composite is abrasive at RT and 200 °C, and a mix of adhesion and delamination at 400 °C, whereas it is a mix of adhesion and oxidation at 600 °C and 800 °C. The Ni_3Al-5Ag-5WS_2 composite reveals abrasive and adhesive wear at RT and 200 °C, adhesion and ploughing at 400 °C, oxidation and delamination at 600 °C, and oxidation with glaze formation at 800 °C.

Chapter 5 contains the results and discussion on the tribological behaviour of Ni_3Al, Ni_3Al-10wt.% Ag, Ni_3Al-10wt.% Cu-*h*BN, and Ni_3Al-5wt.% Ag-5wt.% Cu-*h*BN composites at RT, 200 °C, 400 °C, 600 °C and 800 °C. The addition of Ag and Cu-modified *h*BN nanosheets (Cu-*h*BN) decreases the hardness of Ni_3Al from 355 ± 5 $HV_{0.2}$ to 313 ± 6 $HV_{0.2}$ and 335 ± 5 $HV_{0.2}$, respectively. However, the combined addition of Ag and Cu-modified *h*BN nanosheets (Cu-*h*BN) to Ni_3Al leads to a hardness value of 325 ±7 $HV_{0.2}$. A reduction in the hardness has been ascribed to the soft nature of Ag and *h*BN.

At RT, the coefficient of friction (CoF) for Ni_3Al stabilises after 400 s and maintains a constant value throughout the entire duration of the test with marginal fluctuations in the amplitude, while the CoF for the composites stabilises after 900 s (Ni_3Al-10Ag), 800 s (Ni_3Al-10Cu-*h*BN), and 1000 s (Ni_3Al-5Ag-5Cu-*h*BN), respectively, with minor fluctuations. At 200 °C, the CoF of Ni_3Al, Ni_3Al-10Ag, Ni_3Al-10Cu-*h*BN and Ni_3Al-5Ag-5Cu-*h*BN stabilises after 1400 s, 1000 s, 1200 s and 900 s, respectively. At 400 °C, the CoF for Ni_3Al-5Ag-5Cu-*h*BN appears to be stable right from the beginning to the completion of the test without evidence of any run-in period, whereas the CoF for Ni_3Al, Ni_3Al-10Cu-*h*BN and Ni_3Al-10Ag stabilises after 400 s, 600 s, and 800 s, respectively. However, the fluctuations in amplitude are relatively large at 400 °C compared to those at RT. At 600 °C, the CoF for Ni_3Al and Ni_3Al-10Ag remains steady for the entire duration while the CoF of

Ni_3Al-10Cu-*h*BN and Ni_3Al-5Ag-5Cu-*h*BN stabilises after 1400 s. At 800 °C, the CoF for Ni_3Al, Ni_3Al-10Ag, Ni_3Al-10Cu-*h*BN and Ni_3Al-5Ag-5Cu-*h*BN remains steady for the entire duration, with the occurrence of relatively larger fluctuations in amplitude in Ni_3Al-10Ag and Ni_3Al-5Ag-5Cu-*h*BN than Ni_3Al and Ni_3Al-10Cu-*h*BN.

The average coefficient of friction of Ni_3Al-5Ag-5Cu-*h*BN and Ni_3Al-10Ag has been observed to decrease from 0.41 to 0.19 and from 0.45 to 0.26, respectively, while the coefficient of friction of Ni_3Al and Ni_3Al-10Cu-*h*BN is found to reduce from 0.65 to 0.423 and from 0.48 to 0.279, respectively, with the increase in temperature from RT to 800 °C. A decrease in the coefficient of friction for Ni_3Al-5Ag-5Cu-*h*BN with increasing temperature has been attributed to the occurrence of a synergistic action of Ag and Cu-*h*BN and the formation of lubricous silver molybdates (Ag_2MoO_4 and $Ag_2Mo_2O_7$), *h*BN, CuO, MoO_3, NiO and $NiMoO_4$ at 600 °C and 800 °C as revealed by FESEM-EDS, XRD and Raman analyses.

The wear rate of all composites increases as the temperature is raised from RT to 400°C, followed by a decrease beyond 400 °C (i.e., at 600 °C and 800 °C). However, both the increase and decrease in wear rate with temperature are quite significant for Ni_3Al and Ni_3Al-10Ag, whereas the same is minor for Ni_3Al-10Cu-*h*BN and Ni_3Al-5Ag-5Cu-*h*BN. The wear rate of Ni_3Al, Ni_3Al-10Ag, Ni_3Al-10Cu-*h*BN and Ni_3Al-5Ag-5Cu-*h*BN increased from 3.52 to 5.95×10^{-5} mm^3/Nm, 2.96 to 6.66×10^{-5} mm^3/Nm, 2.285 to 3.1×10^{-5} mm^3/Nm, and 2.185 to 2.95×10^{-5} mm^3/Nm, respectively, as the temperature is raised from RT to 400 °C, followed by a decrease to 2.46×10^{-5} mm^3/Nm, 2.3×10^{-5} mm^3/Nm, 1.95×10^{-5} mm^3/Nm and 1.85×10^{-5} mm^3/Nm at 800°C. Among Ni_3Al, Ni_3Al-10Ag, Ni_3Al-10Cu-*h*BN and Ni_3Al-5Ag-5Cu-*h*BN, the Ni_3Al-5Ag-5Cu-*h*BN composite exhibited the lowest CoF (0.41 to 0.19) and wear rate (2.185 to 1.85×10^{-5} mm^3/Nm) at all temperatures, and this has been ascribed to the synergistic lubrication effect between Ag and Cu-*h*BN from

RT to 800 °C. The improved tribological performance has been attributed to the presence of lubricious species (Ag, *h*BN, Ag_2MoO_4, $Ag_2Mo_2O_7$, NiO, CuO, MoO_3, and $NiMoO_4$) over the worn surface of composites and the counterface ball. At low temperatures, Ag acts as an effective lubricant, whereas *h*BN, Ag_2MoO_4, $Ag_2Mo_2O_7$, NiO, CuO, MoO_3, and $NiMoO_4$ contributed to lowering the coefficient of friction as well as the wear rate at elevated temperatures.

The wear mechanism for Ni_3Al-10Cu-*h*BN composite is abrasive and delamination at RT and 200 °C, which changes to a mix of adhesion and delamination at 400 °C, oxidation and adhesion dominated wear at 600 °C, and tribo-oxidation at 800 °C. For Ni_3Al-5Ag-5Cu-*h*BN composite, the wear mechanism is abrasive, adhesive and ploughing at RT and 200 °C, adhesion and ploughing at 400 °C, adhesion and tribo-oxidation at 600 °C, and oxidation with glaze formation at 800 °C.

This chapter also includes the results and discussion on the tribological behaviour of Ni_3Al, Ni_3Al-10wt.% WS_2, Ni_3Al-10wt.% Cu-*h*BN, and Ni_3Al-5wt.% WS_2-5wt.% Cu-*h*BN composites at RT, 200 °C, 400 °C, 600 °C, and 800 °C. The incorporation of WS_2 enhances the micro-hardness of Ni_3Al from 355 ± 5 $HV_{0.2}$ to 365 ± 6 $HV_{0.2}$, while Cu-*h*BN reduces it to 335 ± 5 $HV_{0.2}$. However, incorporating both WS_2 and Cu-*h*BN leads to an increase in the hardness of Ni_3Al to 358 ± 4 $HV_{0.2}$.

Ni_3Al, Ni_3Al-10WS_2, Ni_3Al-10Cu-*h*BN, and Ni_3Al-5WS_2-5Cu-*h*BN composites have been found to exhibit a fluctuating variation of CoF with test duration. However, Ni_3Al and Ni_3Al-10Cu-*h*BN composites have shown significant fluctuations than Ni_3Al-10WS_2 and Ni_3Al-5WS_2-5Cu-*h*BN due to their relatively lower hardness, which allows the harder asperities of the Si_3N_4 ball to penetrate into the composite. All the materials have shown a continuous decrease in CoF with increasing temperature, and the CoF for Ni_3Al and Ni_3Al-10WS_2 has been found to decrease from 0.65 to 0.42 and 0.42 to 0.24, respectively. Similarly, the CoF for Ni_3Al-10Cu-*h*BN and Ni_3Al-5WS_2-5Cu-*h*BN has been found to reduce from 0.48 to 0.28 and 0.44 to 0.18, respectively, as the temperature changes from RT to 800 °C.

The wear rates of Ni_3Al, Ni_3Al-10WS_2, Ni_3Al-10Cu-*h*BN and Ni_3Al-5WS_2-5Cu-*h*BN composites have been observed to increase from 3.52 to 5.95 × 10^{-5} mm^3/Nm, 1.58 to 2.52 × 10^{-5} mm^3/Nm, 2.285 to 3.1 × 10^{-5} mm^3/Nm, and 2.12 to 2.61 × 10^{-5} mm^3/Nm, respectively, as the temperature is increased from RT to 400 °C followed by a decrease to 2.46 × 10^{-5} mm^3/Nm, 1.06 × 10^{-5} mm^3/Nm, 1.95 × 10^{-5} mm^3/Nm, and 0.875 × 10^{-5} mm^3/Nm, respectively, at 800 °C.

Ni_3Al-5WS_2-5Cu-*h*BN has shown the lowest ($\mu \sim 0.44$ to 0.18, $W \sim 2.61 \times 10^{-5}$ to 0.875×10^{-5} mm^3/Nm) at all the temperatures except at RT, 200 °C, and 400 °C, at which Ni_3Al-10WS_2 has shown a slightly lower CoF and wear rate in comparison to Ni_3Al-5WS_2-5Cu-*h*BN. The improved tribological performance of Ni_3Al-5WS_2-5Cu-*h*BN reflects the cooperative action among CuO, *h*BN, NiO, MoO_3, WO_3 and $NiMoO_4$ in effectively reducing friction and wear at temperatures beyond 400 °C. The wear mechanism for Ni_3Al-5WS_2-5Cu-*h*BN composite is abrasive and delamination at RT and 200 °C, and it is a mix of ploughing, delamination and adhesion at 400 °C, adhesion and tribo-oxidation at 600 °C, and tribo-oxidation with smooth and continuous glaze formation at 800 °C.

Chapter 6 presents the major conclusions of the current investigation pertaining to the elevated temperature friction and wear behaviour of composites and the potential of Cu-*h*BN hybrid as a solid lubricant.