

PREFACE

Tribology is an interdisciplinary field of science and engineering that focuses on understanding the complex interactions between surfaces in motion relative to one another. It involves studying friction, wear, lubrication, and the overall behavior of materials in contact, playing a crucial role in the performance and durability of mechanical systems from everyday devices to advanced industrial machinery. Tribology plays a vital role in improving machinery's efficiency, reducing energy usage, and preventing premature wear and failure, significantly influencing various industries and daily life. Wear, the gradual loss of material from interacting surfaces, is a leading cause of material wastage and decreased mechanical performance. Minimizing wear can lead to substantial cost savings. Friction, a primary contributor to wear and energy loss, is estimated to be in large amount $\sim 1/3$ - $1/2$ of global energy consumption. As a result, considerable resources are dedicated to reducing friction. Lubrication, whether in liquid or solid forms, is a highly effective solution for controlling both the friction and wear.

High temperature lubrication is a critical requirement in various high technology areas encompassing aerospace, automotive, manufacturing, and defense etc. Liquid lubricants are typically limited to temperatures below 350 °C due to their tendency to decompose and degrade rapidly at elevated temperatures. Conversely, certain solid lubricants can endure temperatures up to 1000 °C, making them the only viable solution for reducing friction in applications exceeding 350 °C. Commonly used solid lubricants in industrial applications include soft metals (Au, Ag), layered materials (*h*-BN, MoS₂, WS₂, graphite), metal oxides (CuO, NiO, MoO₃), double oxide phases (Ag₂MoO₄, Ag₂Mo₂O₇), alkaline halides (BaF₂, CaF₂), and MAX phases (Ti₃SiC₂, Ti₂AlC). A low coefficient of friction, high resistance to wear and oxidation qualities are crucial properties for materials

used in a wide range 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.

Nickel is a versatile metal that can form alloys with iron, chromium, aluminium, titanium, tungsten, molybdenum, silver, and cobalt, due to its high solubility. Nickel-based alloys are widely utilized in industrial applications such as gas turbine components, medical devices, and nuclear systems, primarily addressing challenges related to wear resistance, corrosion, and thermal fatigue. Ni-based alloys are particularly used in gas turbine engines, where high temperature lubrication is a challenging task. As a result, it is crucial to develop materials capable of self-lubricating over a broader temperature range. In the present study, Ni alloy-based composites containing Ag and its combinations with other solid lubricants, namely, reduced graphene oxide (rGO), Ni-doped rGO (rGO-Ni), and Ni-doped *h*-BN (*h*-BN-Ni) have been fabricated by Spark Plasma Sintering (SPS) and their tribological performance has been evaluated by carrying out dry sliding wear tests at room temperature (RT), 200, 400, 600, and 800 °C at a constant load of 5 N and sliding speed of 0.5 m/s using a high temperature ball-on-disc 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-rGO, Ag-(rGO-Ni), and Ag-(*h*-BN-Ni) in realizing low friction and wear over the entire range of temperature from RT to 800 °C. The study has been divided into four parts based on the addition of solid lubricants: (i) tribological behaviour of Ni alloy-based composites containing Ag, Ag-rGO, and Ag-(rGO-Ni), (ii) effect of rGO-Ni content on tribological behaviour of Ni alloy-based composites, (iii) tribological behaviour of Ni alloy-based composites containing a fixed amount of Ag, and different amounts of *h*-BN-Ni, and (iv) tribological behaviour of

Ni alloy-based composites containing fixed amounts of Ag, rGO-Ni, and different amounts of *h*-BN-Ni. The thesis has been divided in the eight chapters.

Chapter 1 outlines the introductory remarks emphasizing the technological significance of the issue being investigated.

Chapter 2 begins with a concise overview of composites and their various types, followed by an in-depth review of processing routes for fabricating metal-based composites, with specific emphasis on the spark plasma sintering technique. This chapter also introduces the concept of wear, discussing its types, influencing factors, and both solid and liquid lubrication. The importance of solid lubrication is emphasized, along with a brief description of different types of solid lubricants. The chapter also sheds a light on the structure of high temperature solid-lubricating materials and then offers a comprehensive literature review on the tribological behaviour of Ni alloy-based high temperature solid lubricating composites with special emphasis on Nickel alloy matrix composites and their wear mechanisms observed under dry sliding of these composites at temperatures from room temperature up to 800 °C. The chapter concludes with a statement 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 rGO, Ni-doped rGO (rGO-Ni) and Ni alloy-based composites. Details of experimental procedures and machines/instruments for fabrication, testing, and characterization of the composites and their worn surfaces have been included in the Chapter. 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 (FESEM) and Energy Dispersive X-ray analysis (EDS) 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 behaviour has been evaluated by carrying out dry sliding tribo-tests using a ball-on-disc rotary tribometer (DUCOM, India) with a Si_3N_4 ball as a stationary counterpart. 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 EDS, X-ray diffraction and Raman spectroscopy to reveal the presence of different species and explore the wear mechanisms.

Chapter 4 includes the results and discussion on the characterization of rGO and Ni-doped rGO via high resolution TEM, XPS, XRD and Raman spectroscopy. It is followed by the characterization of ball milled powder(s) and SPS sintered Ni alloy-based composites reinforced with 10 wt. % Ag, and the combination of 10 wt.% Ag with 1 wt. % rGO and 1 wt.% Ni-rGO, designated as NA, NAG, and NANG, respectively. Microstructural features of the prepared composites have been analysed by using SEM, while phase confirmation has been done using XRD. The hardness of Ni Alloy (N0) has been found to reduce from 515 ± 5 to 497 ± 4 , 503 ± 6 and 510 ± 3 $\text{HV}_{0.3}$ with the incorporation of 10 wt.% Ag for NA, 1 wt.% rGO along with 10 wt.% Ag for NAG, 1 wt.% rGO-Ni and 10 wt.% Ag for NANG, respectively. The increased hardness of NANG compared to NAG has been credited to the uniform distribution of rGO-Ni in the matrix caused by enhanced wetting characteristics of rGO-Ni with the matrix.

The average CoF for N0 and NA has been found to decrease from RT to 800 °C. However, the CoF for NAG and NANG decreased from RT to 600 °C followed by slight increase at 800 °C. The variation in CoF with increasing temperature has been attributed to the presence of a transfer layer containing solid lubricants Ag at relatively low temperatures and the existence of lubricious oxides (NiO , MoO_3 , Ag_2MoO_4 , $\text{Ag}_2\text{Mo}_2\text{O}_7$ and NiMoO_4) at elevated temperatures on the worn surface of the composites. The wear rate of N0 has been

found to increase from RT to 600 °C followed by a decrease at 800 °C whereas the same for NA has been observed to increase with increasing temperature from RT to 400 °C and decrease thereafter till 800 °C. The wear rate of NAG has been observed to increase from RT to 200 °C followed by a decrease till 800 °C. The wear rate of NANG is found to increase from RT to 200 °C and decrease at 600 °C before increasing again at 800 °C. The observed variation has been explained on the basis of morphology of the worn surfaces of the composites and presence of lubricious oxides (NiO, MoO₃, Ag₂MoO₄, Ag₂Mo₂O₇, and NiMoO₄). NANG has shown the lowest CoF and wear rate from RT to 600 °C, which has been attributed to the occurrence of a synergistic action between Ag and rGO-Ni. However, an increased CoF at 800 °C for NAG and NANG has been credited to the possible loss of assistive action between Ag and rGO/rGO-Ni.

The dominant wear mechanisms for N0 and NA have been found to be ploughing and delamination from RT to 400 °C, which changes to oxidative wear at 600 and 800 °C. However, the wear mechanisms for NAG and NANG are ploughing and delamination from RT to 200 °C, delamination at 400 °C and a combination of abrasion and oxidation at 600 and 800 °C as revealed by the worn surface morphologies at these temperatures.

Chapter 5 presents the results and discussion on the characterization of ball milled powders and SPS sintered Ni alloy-based composites containing combination of fixed amount of Ag (10 wt.%) with different amounts of Ni-doped rGO (0.5, 1.0, 1.5, and 2.0 wt.%) namely NANG0.5, NANG1.0, NANG1.5, and NANG2.0, respectively. The addition of rGO-Ni (0.5-2.0 wt.%) in NA has been found to result in an increase in the hardness from 496 ± 4 to 517 ± 1 HV_{0.2}. The average CoF for NANG0.5, NANG1.0, and NANG1.5 has been found to decrease significantly from RT to 200 °C before increasing marginally at 400 °C and decreasing slightly at 600 °C followed by an increase at 800°C. However, the

CoF for NANG2.0 remained almost stable from 200 to 800 °C after a decrease from RT to 200 °C and it has shown the lowest CoF in comparison to other materials at all the temperatures except 800 °C. The variation of CoF with temperature for composites has again been explained on the morphological features seen on the worn surface of these composites depending on temperature, presence of the transfer layer containing lubricious oxides and the relative dominance of decreasing hardness due to softening of material with increasing temperature and efficacy of lubricious species. The decrease in CoF of the composites containing Ag and rGO with increasing amount of rGO has been attributed to the presence a relatively larger amount of lubricating rGO apart from the increasing hardness with an increasing amount of rGO.

The wear rate for NANG0.5, NANG1.0, and NANG1.5 has been observed to increase marginally with increasing temperature from RT to 200 °C which is followed by a decrease to 600 °C before increasing again at 800 °C. However, the wear rate of NANG2.0 is found to remain almost the same from RT to 200 °C with a slight decrease thereafter to 600 °C and a sharp increase at 800 °C. The observed behaviour has been explained on the basis of the presence of salient features seen on the worn surface of the composites like the presence and nature of transfer layer, the extent of the coverage provided by this layer and the availability of lubricious compounds. The wear rate of the composites has been observed to decrease with an increasing amount of rGO, which has been ascribed to the presence of a relatively larger amount of rGO available for lubrication in addition to the increased hardness with increasing rGO. The dominant wear mechanisms for NANG0.5, NANG1.0, and NANG1.5 are ploughing and delamination from RT to 200 °C, delamination at 400 °C and a combination of abrasion and oxidation at 600 and 800 °C. However, the wear mechanisms for NANG2.0 are a combination of ploughing and abrasion from RT to 600 °C, whereas the same is oxidative at 800 °C.

Chapter 6 includes the results and discussion on the characterization of ball milled powders and composites containing a combination of fixed amount of Ag (10 wt.%) with different amounts of *h*-BN (2, 4, 6, and 8 wt.%), namely, NAh2, NAh4, NAh6, and NAh8, respectively. An increase in the amount of *h*-BN has been found reduce the hardness from 405 ± 3 to 313 ± 2 HV_{0.3} which has been attributed to the poor sintering and wetting characteristics of *h*-BN despite the fact that *h*-BN has been modified by Ni with an aim to improve these features. The other contributing factor is the agglomeration of *h*-BN in composites containing a relatively higher content viz. 6 and 8 wt. % *h*-BN.

The average CoF for all the composites i.e., NAh2, NAh4, NAh6, and NAh8 has been found to decrease with increasing temperature as well as the amount of addition of *h*-BN-Ni. This has been credited to the occurrence of a synergistic action between Ag and *h*-BN and the presence of lubricious compounds on the worn surface of composites. The decrease in CoF in composites at all the temperatures has been credited to the increasing amount of *h*-BN. The wear rate for the composites, i.e., NAh2, NAh4, NAh6, and NAh8 has been found to increase from RT to 400 °C, which is followed by a decrease at 600 and 800 °C. At a particular temperature, the wear rate of the composites has been observed to decrease with the addition of *h*-BN from 2 and 4 wt.%, whereas the addition of 6 and 8 wt.% has resulted in an increase in the wear rate. The observed behaviour has been explained on the basis of the characteristic features of the transfer layer present on the worn surfaces of composites apart from the synergistic action of Ag and *h*-BN and the relative dominance of reducing hardness and the lubricating efficacy of the combination of lubricants. The dominant wear mechanism for all the composites has been found to be ploughing at RT and a combination of abrasion and ploughing at 200 and 400 °C, whereas it is observed to be oxidative at 600 and 800 °C.

Chapter 7 presents the results and discussion on the characterization of ball milled powders and composites containing a novel combination of Ag (10 wt.%), rGO (1 wt.%) and Ni-doped *h*-BN (2, 4, 6, and 8 wt.%) designated as NANGh2, NANGh4, NANGh6, and NANGh8, respectively. An increase in the amount from 2 to 8 wt.% of Ni-doped *h*-BN has been found to decrease the hardness of the composites from 458 ± 3 to 412 ± 2 HV_{0.3}, which has been attributed to the inherent softness of *h*-BN. The CoF of composites has been found to decrease with increasing content of *h*-BN from 2 to 8 wt.% with a marginal change in wear rate at all the temperatures. However, NANGh8 has shown the lowest CoF (~ 0.27-0.17) at all the temperatures. The decrease in CoF with increasing temperature has been ascribed to the presence of tribo-layer containing lubricating components i.e., Ag, *h*-BN, NiO, MoO₃, NiMoO₄, Ag₂MoO₄, and Ag₂Mo₂O₇ depending upon temperature as confirmed by the XRD and the Raman spectra which endows the interface with easy shearing capability and helps in restricting the junction growth despite their low hardness.

The wear rates for NANGh2, NANGh4, NANGh6, and NANGh8 have been observed to lie in a narrow band with NANGh6 showing the lowest wear rate than others at all the temperatures. The decrease in wear rate at 800 °C despite a reduction in the hardness due to softening indicates the dominating effect of the glazed layer over the decreasing hardness.

A combination of abrasion and ploughing at RT and 200 °C, delamination, ploughing, and oxidation at 400 °C, whereas oxidation at 600 and 800 °C have been found to be the dominant mechanisms of wear.

Chapter 8 presents the salient conclusions on the microstructural, mechanical and tribological characteristics of Ni-alloy based composites fabricated in the present investigation along with the future scope of the study.