

Chapter 2: Review of literature

The chapter begins with a brief description on the composites, their types and techniques used to fabricate the composites with special emphasis on vacuum hot press sintering (VHPS). 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-alloy 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 lubricants. The chapter also highlights the relevant research gap identified based on the critical assessment of the literature and ends with the problem formulation and the major research objectives.

2.1 Composite and its types

Composite materials are formed through the integration of a minimum of two components that possess distinct physical properties and can be chemically separated if necessary. The materials comprise a primary phase referred to as the matrix, which is continuous, and a secondary phase known as the reinforcement, which is discontinuous and present in smaller quantities. The primary objective behind the development of composites is to attain distinct properties that are unattainable with a single, homogeneous material. The categorization of composites is determined by three primary factors: (i) the matrix type, which includes metal, polymer, or ceramic, (ii) the characteristics of the reinforcing phase, such as long or short fibres, whiskers, or particulates, and (iii) the configuration of the

reinforcement, which can take the form of continuous fibres, discontinuous fibres, or wires.

The classification of composites based on the matrix is illustrated in Fig. 2.1.

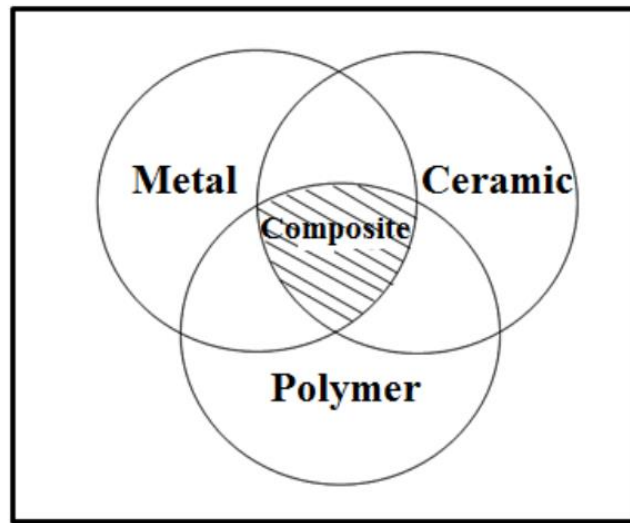


Fig. 2.1: Matrix based classification of composites. [1]

Metal matrix composites (MMCs) are widely used in various applications due to their exceptional characteristics, including elevated toughness, high specific modulus, superior thermal conductivity, and reduced thermal coefficient of expansion, among others. A comparison of polymer matrix composites (PMCs) and metal matrix composites (MMCs) suggests that the latter exhibit superior fire resistance, elevated temperature tolerance, increased transverse strength, enhanced stiffness, high shear strength, and improved compressive strength. Also, MMCs possess several advantages over ceramic matrix composites (CMCs), including enhanced toughness, resistance to moisture, high electrical and thermal conductivity, resistance to thermal shock, and ease of fabrication in terms of joining, shaping, and manufacturing.

2.1.1 Processing techniques for composites

A wide variety of processing techniques are used to fabricate MMCs. The outcome is primarily contingent upon the condition of the matrix material during the processing

stage. The aforementioned processes can be categorized into five primary classifications, as depicted in Fig. 2.2.

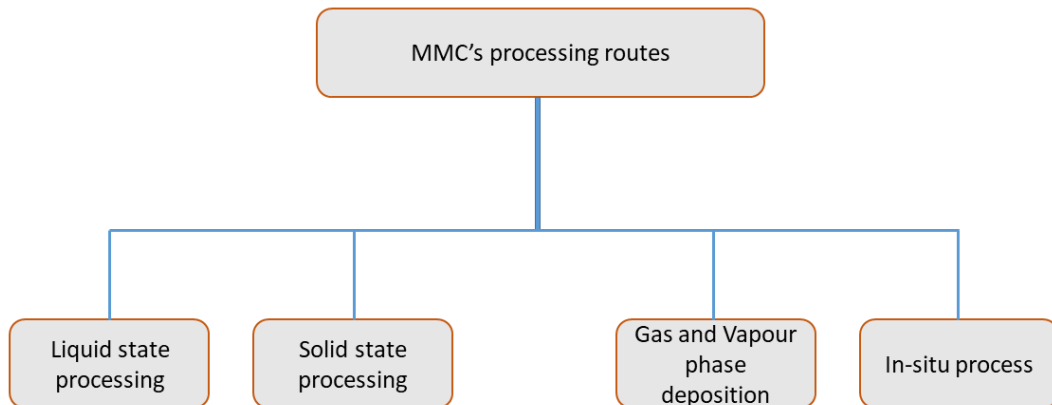


Fig. 2.2: Classification of the processing routes to develop MMCs.

2.1.1.1 Liquid State Processing

Composite preparation via **liquid state processing** involves incorporating particles of reinforcing phase into molten metal, followed by mixing and casting the melt. The liquid state processing has been subdivided into three distinct categories: **melt stirring**, **gas pressure infiltration** and **squeeze casting**. In the **melt stirring technique**, reinforcing phase is introduced to molten metal and blended with the aid of a stirrer before being allowed to solidify. It is a straightforward method for preparing composites, but elevated temperatures can degrade the quality of the reinforcement phase. **Gas pressure infiltration** is another kind of liquid state processing in which molten metal is injected under high gas pressure into a ceramic preform. In comparison to other methods of liquid state processing, this one offers the added benefit of producing a pore-free casting. **Squeeze casting** is another sort of liquid state processing technique in which the preform is held at the bottom fixed section of the setup, and molten metal is squeezed into it using pressure from ram displacement. The **in-situ processes** can be categorised into two main groups: (i) controlled solidification of melts [2–5] and (ii) chemical reaction between two phases [6–10]. The

major advantage of in-situ composite materials is that the reinforcing phase is generally homogeneously distributed, and the spacing or size of the reinforcement may be adjusted in several cases by the solidification or reaction time. The interfaces are clean, mutually compatible and coherent because the constituent phase crystallizes in situ rather than combined from separate sources. However, the system selection and the reinforcement orientation are limited, and the process kinetics (in the case of reactions), or the shape of the reinforcing phases, is sometimes difficult to control, as indicated by [11].

2.1.1.2 Solid State Processing

In this process, metal is reinforced with particulates with a mixture of blended elemental powders. There are certain steps involved in this process prior to the final consolidation, and powder metallurgy and diffusion bonding fall under this category.

(i) Powder Metallurgy (P/M)

The powder metallurgy technique involves blending matrix and reinforcements in powdered form in the right proportions, followed by compaction under pressure and sintering at elevated temperatures to facilitate diffusion. The steps involved in the process of preparing a composite using the powder metallurgy (P/M) technique are illustrated in Fig. 2.3. The method offers a versatile means of integrating various types and forms of reinforcement, such as whiskers, fibres, or particulates. The process is characterized by its high versatility, allowing the combination of dissimilar materials, which cannot be achieved by any other process.

Mixing and Blending: Mixing is performed in order to achieve a uniform distribution of all constituent phases. It involves blending elementary powders to form a homogeneous mixture of secondary powder with powder particulates that are properly sized, well distributed and possess a well-defined morphology. To reduce friction and wear during compaction, lubricants are also added to the powders, as abrasive or hard particles can

otherwise abrade the die surface. The mixing and blending process is affected by several parameters, such as milling time, milling vial and ball material, milling environment, ball-to-powder ratio, processing control agent, and ball size. Among these, the mixing time is particularly critical. Excessive mixing should be avoided, as it can lead to the hardening of particles and negatively impact the quality of the composite.

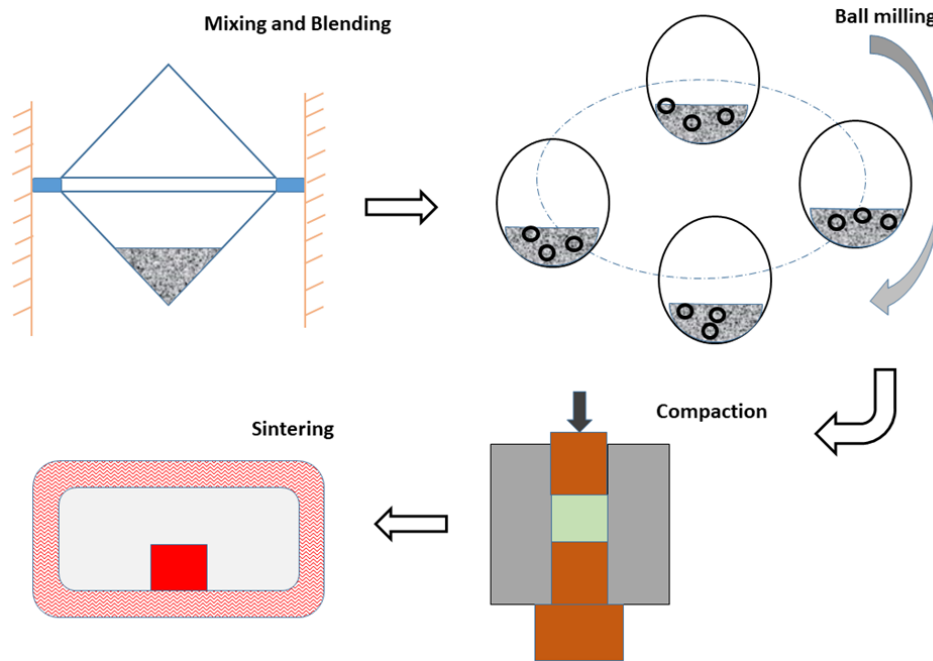


Fig. 2.3: Steps involved in powder metallurgy process.

High-energy ball milling is widely utilized as the predominant mixing method due to its superior efficiency and effectiveness in achieving uniform dispersion of small reinforcement phase particles within the matrix phase. The planetary ball mill is commonly used in mixing processes to reduce the size of powder particles while also facilitating their thorough mixing. The system comprises a jar that is affixed to an eccentric sun wheel. Both the jar and the sun wheel rotate in opposite directions, effectively coordinating the alternating centrifugal force.

Compaction: Compaction refers to the process of compacting a mixture of powders within a die through the application of substantial pressure at ambient temperature, resulting in the

formation of a green compact. This process imparts green strength to the compacts by allowing particles to slide, interlock and undergo plastic deformation. The relationship between compaction pressure and the properties of compact density and porosity is such that as the compaction pressure increases, the density of the compact increases while the porosity decreases [12].

Sintering: During this process, the compacts are subjected to heat in order to facilitate the fusing of pores between the interlocking particles, leading to an improvement in both density and strength. The process consists of three stages. In the initial stage, interparticle welding occurs among loosely arranged particles, and the weld enlarges as the sintering time progresses [13]. In the second stage, the network of pores becomes unstable and begins to contract, followed by the third stage, where the pores disappear. Fig. 2.4 illustrates the various sintering stages and the associated diffusion that occurs in the process.

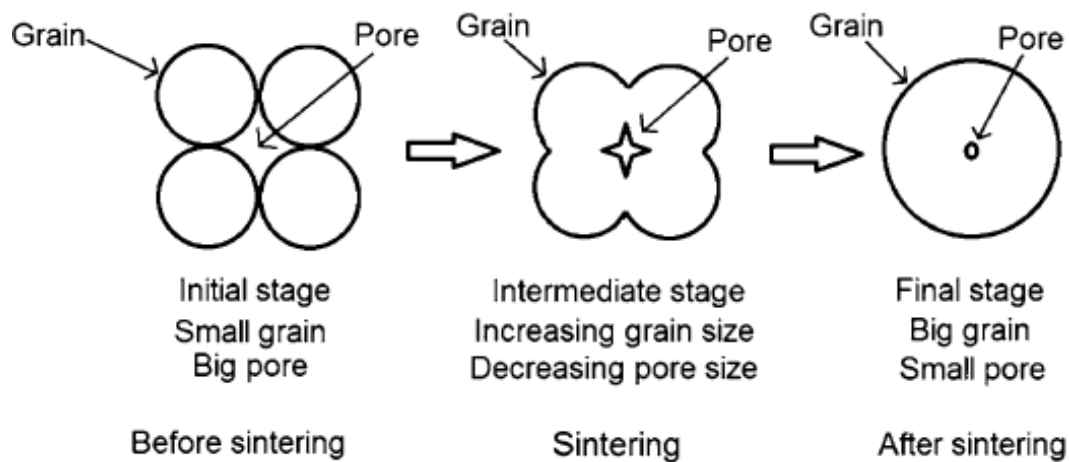


Fig. 2.4: A schematic diagram of sintering. [14]

A number of sintering techniques, such as conventional sintering, microwave sintering, spark plasma sintering and vacuum hot press sintering have been utilised in the fabrication of composite materials. The **conventional sintering process** involves heating preformed powders to a temperature below their melting point for a period of time ranging from several minutes to hours. This is done to facilitate diffusion. **Microwave sintering** is commonly linked to dielectric properties, which serve as indicators of a material's response

to microwave irradiation. **Spark plasma sintering** process involves the occurrence of joule heating and the application of a simultaneous load throughout the consolidation process. The process of sintering takes place at temperatures considerably lower than the melting point. **Vacuum Hot Press Sintering (VHPS)** is a specialized method to consolidate powder or particulate materials into dense, uniform, and structurally sound forms. What sets VHPS apart from conventional sintering techniques is its operation within a controlled vacuum or low-pressure environment, which eliminates the presence of unwanted gases and contaminants. This controlled atmosphere ensures the production of pristine and high-purity materials. The core principle of VHPS revolves around the application of simultaneous high temperatures and pressures to the material being processed. This process offers numerous advantages compared to spark plasma sintering, such as operation at high pressure and temperature levels, longer sintering times, large chamber sizes to handle significant sample volumes, uniform heating and cooling throughout the sample, and versatility in processing a wide range of materials (refractory metals, intermetallic compounds, and ceramics) under different conditions.

(ii) **Diffusion bonding**

It is a solid-state processing in which fibres and metal sheets/foils are embedded alternatively to form a sandwich structure. The foil and fibre sandwich is then compressed and heated above the melting point of foil material, thus wetting the fibre and spreading the metal all over the structure.

2.1.1.3 Gas and Vapor Phase Deposition

Gas and vapour phase techniques can be classified into two main categories: spray and vapour deposition processes. Gas and vapour phase techniques can be classified into two main categories: spray and vapour deposition processes. In **Spray Deposition**, a high-speed cold inert gas (argon or nitrogen) jet is used in the spray deposition processes to

fragment a stream of molten metal into fine droplets (300 μm or less). These droplets are sprayed with reinforcement particles and collected on a substrate or mould, where the semisolid metal droplets recombine and solidify to produce the composite material. The droplets get flattened on impacting the substrate when they strike at very high velocities in molten or partially solidified state and weld together to form the composite. The spray process can be regarded as a hybrid rapid solidification technique, given that the metal undergoes a rapid transformation from the liquid state to the solid state, followed by a slower cooling from the solid state to room temperature, as noted in [15,16]. **EB/PVD (Electron Beam/Physical Vapour Deposition)** involves the passage of fibres through a region characterised by a high partial pressure of the melt deposit. This process facilitates condensation, resulting in the production of a relatively thick coating on the substrate [17–19]. This technique allows for the utilisation of multiple evaporation sources, enabling the variation of composition by effectively controlling the evaporation rate of these sources. There are various advantages of vapour phase deposition like high range of compositions can be prepared, there is no mechanical disturbance of interfacial region, uniform thickness can be achieved and thickness can be controlled. There are currently two prominent vapour deposition techniques that are widely utilised in the market: physical vapour deposition (PVD) and chemical vapour deposition (CVD). **Physical vapour deposition (PVD)** is a vacuum deposition technique that involves the transformation of material from a condensed phase to a vapour phase, followed by its recondensation as a film onto a substrate. On the other hand, **chemical vapour deposition (CVD)** is a process that involves the vaporisation of solid materials, which are then deposited onto a substrate in the form of a thin film through a chemical reaction.

2.2 Tribology

Tribology is a multidisciplinary science and engineering field that examines and comprehends the intricate interactions between surfaces in relative motion [20]. 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 [21]. 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 [22]. Friction is a common occurrence in everyday life and various industrial applications, and the management of friction can enhance machinery efficiency while minimizing energy loss. The loss of material from a surface can result in substantial damage and breakdown of machine parts [23]. 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 [24]. A significant portion of global resources is 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. Hence, for the survival of a machine, wear and friction must either be reduced or controlled [20]. The most prevalent method for decreasing friction, minimizing wear, and preventing catastrophic failure in machine components or the machine as a whole involves carefully choosing materials, lubricants, and employing surface modification techniques.

2.3 Wear and types of wear

Wear refers to the gradual removal of material from a surface due to friction and mechanical interactions between two solid surfaces in motion [22]. Wear can be categorized by considering different elements, including the visual changes in worn parts or

mechanisms and the specific conditions under which material is removed. The types of wear based on these mechanisms and conditions include (i) adhesive wear, (ii) abrasive wear, (iii) erosive wear, (iv) fatigue wear, (v) fretting wear, and (vi) corrosive wear.

Adhesive wear is a type of wear mechanism that occurs when two solid surfaces come into direct contact and adhere to each other, leading to the transfer of material from one surface to the other. This phenomenon results from the strong intermolecular forces between the surfaces, causing them to bond and, as a consequence, experience material loss or deformation. Adhesive wear is often associated with high levels of friction and can cause surface damage and wear-related issues in various mechanical systems and components.

Abrasive wear is a type of mechanical wear that occurs when two surfaces come into contact and one surface wears away or erodes the other due to the presence of abrasive particles or materials. This type of wear is typically characterized by the removal of material from a solid surface as a result of the mechanical action of abrasive substances, which can be in the form of particles, grit, or abrasive tools. Abrasive wear can be caused by various factors, such as the relative motion between two surfaces, the hardness and sharpness of the abrasive particles, and the applied pressure. It is a common form of wear in industries like manufacturing, mining, and machining, and it can lead to the degradation and reduced lifespan of components and machinery.

Erosive wear is a type of mechanical wear that occurs when solid particles, liquids, or gases impinge on a material's surface at high velocity, causing the removal of material through a combination of mechanical and chemical processes. This type of wear is often associated with abrasive particles or slurries carried by a fluid (such as water or air) that come into contact with a material's surface. Erosive wear can be particularly damaging when the impacting particles are hard or sharp, leading to the erosion and degradation of the material over time.

Fatigue wear also known as fatigue failure or damage, occurs when a material experiences repeated loading and unloading cycles over time, leading to progressive and localized structural damage. This type of wear is particularly common in materials subjected to cyclic stress or mechanical vibrations. Fatigue wear is a gradual process that often starts with the formation of microscopic cracks that grow and eventually lead to material failure.

Fretting wear is the material loss due to cyclic rubbing of two surfaces at very low amplitude. It can cause cracks on the surface and lead to catastrophic failure.

Corrosive wear results from the combined action of both mechanical wear and chemical corrosion. In corrosive wear, the material is not only subjected to mechanical forces but also exposed to corrosive substances, such as chemicals, moisture, or aggressive environments, which accelerate the degradation of the material. This combination of mechanical and chemical attacks can lead to accelerated wear and reduced material lifespan.

2.3.1 Factors affecting wear

Wear depends on the **nominal contact pressure** between the sliding surfaces, and transitions are commonly induced by changes in contact pressure. The **linear dimensions of the specimen** are also important, independently of the contact pressure, since wear debris formed near the leading edge of a long specimen will have more influence during its passage through the contact zone than it would have with a shorter specimen. Apart from the major variables of **normal load, contact area, sliding speed and testing time**, several other factors like test temperature, environment, orientation of apparatus, etc., also have a profound effect on the wear of materials. The **testing temperature** is important through its influence on the mechanical properties of the materials and on thermally activated chemical processes, although these may often be dominated by frictionally generated temperature

rise. **Atmospheric composition** is extremely important; reactive components such as water vapour and oxygen strongly influence wear rates and mechanisms in all classes of material. The **orientation of the apparatus** affects the results of testing: different behaviour may be seen if wear debris falls readily away from the contact area under gravity rather than being retained in the counterface.

The amount of material removed from a sliding body depends on the distance slid and on the nominal pressure (normal load divided by the nominal contact area) over the contact region. Wear under sliding conditions depends on the distance slid and to some extent on both the sliding velocity and the duration of the test independently. The sliding velocity affects the rate of frictional energy dissipation and hence the temperature at the interface. It certainly cannot be assumed that one wear test will produce the same results as another of half the duration at twice the sliding velocity, since abrupt transitions in wear mechanism and rate may occur as the sliding speed is changed. It is found by experiments that for many systems, the loss of material by wear is indeed proportional to the sliding distance (and so, for sliding at constant velocity, to the time).

The proportionality between the wear rate and the normal load, as suggested by Archard [25] is less often found. Although for many systems the wear rate varies directly with load over limited ranges, abrupt transitions from low to high wear rate, and sometimes back again, are often found with increasing load. Transitions in the dominant wear mechanism and in the associated rate of wear are commonly seen with a variation of normal load and sliding velocity, and also in some cases with sliding time (or distance). The main factors controlling the importance of the underlying mechanisms are **mechanical stresses, temperature and oxidation phenomena**. Consideration of all three factors is essential in understanding the sliding wear of metals; it must also be appreciated that the conditions at

the interface may be very different, especially in terms of temperature, from those in the surroundings.

The complexity of sliding wear arises from the fact that all three controlling factors are interrelated, and may be influenced by both load and sliding velocity. Increasing the load leads directly to higher stresses and more severe mechanical damage. Both the load and the sliding velocity influence the interface temperature. Together, they control the power dissipated at the interface (since that is the product of the sliding speed and the frictional force). Additionally, the sliding velocity also determines the relative importance of heat conduction away from the interface. At low sliding velocity, because the heat generated will be relatively rapidly conducted away, the interface temperature will remain low; in the limit, the sliding process would be isothermal. At high velocity, only limited heat conduction can occur, the interface temperature is therefore high, and the limiting conditions would be adiabatic. A high interface temperature leads to high chemical reactivity of the surfaces, causing, for example, rapid growth of oxide films in air. The effect of oxide films, whether containing lubricious compounds or not, on wear is complex and context-dependent. Generally, oxide films act as protective barriers, reducing wear by preventing direct contact between surfaces and lowering friction. The presence of lubricious compounds within oxide films can enhance these protective effects. However, specific circumstances, such as high temperatures, may lead to the breakdown of oxide layers, potentially increasing wear. The overall effect depends on factors such as material type, environment, and load. A nuanced understanding of these conditions is crucial for making accurate predictions.

2.4 Lubrication

Lubrication serves the purpose of controlling friction and minimising wear by forming a thin protective film that diminishes the friction between surfaces that are in

contact and in motion. There are several lubrication mechanisms that can be utilised to tackle the diverse challenges faced in technological advancements. These mechanisms include liquid, solid, semi-solid, and gas lubrication.

2.4.1 Liquid lubrication

Liquid lubrication is utilised for the purposes of controlling friction, dissipating excessive heat produced by the system, and minimising wear. The lubricating fluids should possess the ability to expel heat generated by friction and the abrasion of wear particles from the load-carrying area promptly upon its formation. The most common types of liquid lubricants are mineral oil and synthetic oils. Cameron et al. [26] discussed several mechanisms used to facilitate lubrication between two surfaces in contact. One such mechanism is **hydrodynamic lubrication**, in which the sliding surfaces are separated by a dense lubricant film owing to the pressure of the fluid lubricant. The pressure generated by the thick film lubricant supports the normal load hydrodynamically. When the contacting surfaces involve line or point contact, such as gear teeth, cam and follower, or ball on disc, the local pressure at the point of contact is significantly higher compared to hydrodynamic lubrication. In this context, the relationship between lubricant viscosity and pressure is crucial for ensuring effective lubrication. The lubrication that occurs in such conditions is referred to as **Elastohydrodynamic lubrication (EHL)**. In situations where there are extremely high contact pressures or very low sliding speeds, the hydrodynamic forces are not strong enough to sustain a thin Elastohydrodynamic (EHL) film between the two surfaces in contact. In such cases, the **boundary lubrication** mechanism is responsible for providing adequate lubrication. Boundary lubrication is less effective in reducing friction and wear compared to hydrodynamic lubrication, where a thick fluid film separates the surfaces. However, it plays a critical role in protecting surfaces in situations where other

lubrication mechanisms may not be sufficient to prevent damage, such as during initial engine startup or in applications with heavy loads and low relative speeds.

Liquid lubricants, despite their usefulness, have certain limitations that restrict their application in specific conditions. Certain applications may not be suitable for their use due to challenges in application, sealing issues, weight constraints, or other factors. When exposed to high temperatures, liquid lubricants can decompose or oxidise, resulting in a decrease in viscosity and a deterioration in performance. On the other hand, liquid lubricants are prone to contamination in corrosive environments, unlike most solid lubricants.

2.4.2 Solid lubrication

In certain conditions, liquid lubricants do not possess the capability to offer superior tribological characteristics. Consequently, the integration of solid lubricants into various matrices has been pursued in order to improve the reliability and self-adjusting capabilities of lubricating materials, with the aim of achieving adequate lubrication. Solid lubricants exhibit excellent lubrication properties primarily due to their ability to shear across the mating surface. The effectiveness of their lubricating behaviour can be attributed to their layered structure. When subjected to an external force, these layers align themselves in parallel to the direction of the force and subsequently glide over one another. This action effectively diminishes the friction that occurs between surfaces during their relative motion. Solid lubricants such as soft metals, transition metal dichalcogenides (TMDs), metal oxides, fluorides, hexagonal boron nitride (*h*-BN), and polymers are the most common types of lubricants that are utilised in self-lubricating materials [27–31].

Soft metals, including Ag, Sn, Au, Pb, In and Pt contain multiple slip planes and demonstrate unique properties such as a low coefficient of friction (CoF) across a wide range of temperatures. These distinctive characteristics result from the inherent properties

of soft metals, including low surface roughness and high viscosity. In soft metals, the heat generated through friction during sliding serves to eliminate lattice defects, like dislocations and vacancies [29]. This elimination of lattice defects results in improper work hardening, which is the key factor contributing to superior lubrication in challenging conditions.

Silver (Ag) is the preferred choice among soft metals for self-lubricating materials in demanding conditions, primarily due to its superior oxidation resistance and high thermal conductivity, enabling efficient dissipation of heat generated during relative motion. The primary self-lubrication mechanism of silver is its exceptional diffusion and the facile formation of a tribo-layer at the interface. Consequently, silver is capable of delivering superior lubrication properties when operating at temperatures below 500 °C [32]. The most commonly utilised **Transition Metal Dichalcogenides (TMDs)** include molybdenum disulfide (MoS₂) and tungsten disulfide (WS₂). TMDs feature a layered structure that facilitates easy shearing during relative motion, offering excellent lubrication characteristics up to 400 °C [33]. MoS₂ is not suitable for self-lubrication in humid or moist environments due to the oxidation reaction it undergoes. The resulting oxide has higher shear strength, leading to subpar tribological properties. On the other hand, WS₂ can endure temperatures up to 500 °C and provides superior lubrication properties [34,35]. **Metal oxides** are known for their thermal stability at high temperatures (HT) and are effective lubricants. However, they do not possess lubricating properties at room temperature (RT). Many oxides exhibit a change in tribological behaviour as the temperature increases. The observed changes in tribological properties can be attributed to the transition from brittle to ductile behaviour, which occurs when the temperature exceeds a critical threshold. Hence, temperature significantly influences oxide lubrication.

Inorganic fluorides such as BaF₂, CaF₂, CeF₃, LaF₃ and LiF exhibit significantly better tribological properties above 500 °C but perform poorly at low temperatures and room temperature. The main reason for their excellent lubricating properties at high temperatures is the shift from a brittle to a ductile wear mechanism, while the higher coefficient of friction and increased wear rate are attributed to three-body abrasion. CaF₂ and BaF₂, being soft, poorly soluble in water, and thermally stable across a wide temperature range, have a thermal expansion coefficient that closely matches that of many alloys.[29,31]

Hexagonal boron nitride (*h*-BN) powder is soft, white and lubricious with unique characteristics that make it an attractive, performance-enhancing alternative to graphite, molybdenum disulfide and other commonly used inorganic solid lubricants [36–38]. With its superior adherence and thermo-chemical stability, *h*-BN presents an opportunity to formulate new solid lubricants for applications where conventional solid lubricants break down or fail to deliver the desired performance. This inorganic solid powder retains its ability to lubricate in extreme cold or heat and is well suited to extreme pressure (EP) applications. **Polymers** like polyimide (PI), polytetrafluoroethylene (PTFE), and polyetheretherketone (PEEK) are excellent additives for solid lubrication in a cryogenic environment and possess superior tribological characteristics [39,40]. **Carbon and carbon-based materials** like graphite, diamond-like carbon (DLC), graphene, graphene nanoplatelets (GNP), multi-layered graphene (MLG) and carbon nanotubes (single and multi-walled) are utilised as additives in self-lubricating materials for challenging environments [24,41–44]. Among these, graphene has gained tremendous attention due to its unique properties, such as high chemical inertness, high thermal conductivity, low shear strength, and enhanced mechanical and thermal properties. Graphene is a two-dimensional material capable of providing low friction and wear properties, and is the fundamental

building block of graphite. The superior tribological properties possessed by graphite can be correlated to its layered structure, similar to MoS₂, MoSe₂, and WS₂, which provides easy shearing and reduces the friction between contact surfaces in relative motion. Fig. 2.5 represents the typical solid lubricants used for self-lubricating materials in challenging environments.

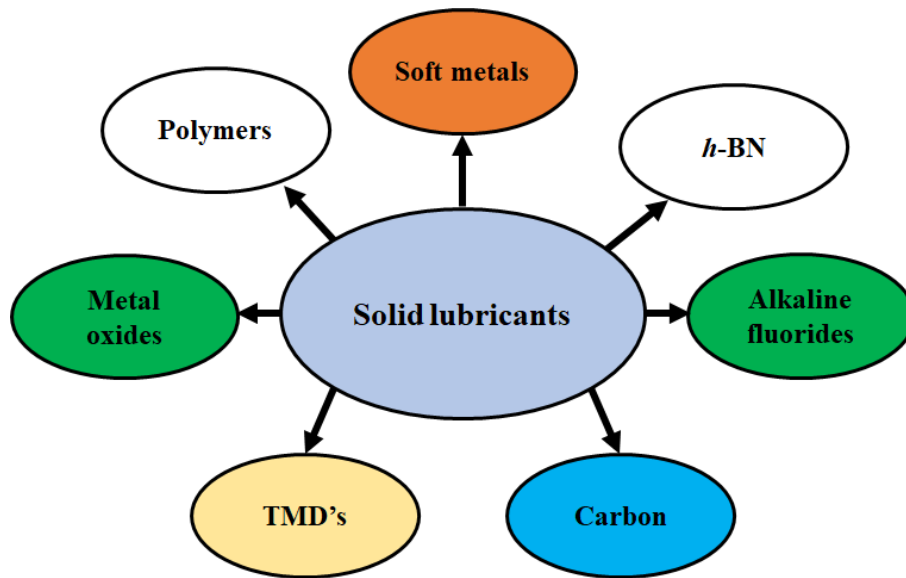


Fig. 2.5: Typical solid lubricants

2.4.3 Need for solid lubrication

With the advancements in technology, it has become necessary for the essential components of moving assemblies to operate continuously under harsh conditions of load, speed, temperature, and environment. Considering the demands and obstacles posed by contemporary technology, the utilisation of solid lubricants has emerged as the most important practical solution for minimising friction in various challenging environments. This is particularly true for situations involving temperatures exceeding 350 °C, where the lubricating efficacy of liquid and polymer lubricants diminishes, rendering them ineffective. Traditional solid lubricants, such as graphite and MoS₂, demonstrate insufficient lubrication capabilities when subjected to temperatures exceeding 500 °C

[27,31]. In specific conditions, such as food processing plants where the use of liquid lubricants can lead to contamination, or in environments like space where liquid lubricants may vaporise, solid lubrication becomes the most viable option for combating high-load conditions, machinery components that are challenging to access, environments with excessive dust or lint, and instances when loading is inconsistent [29]. 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 [28,29,45,46]. These applications include components for turbine engines, aerospace technologies, automobile engines, and cutting tools. 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 or coatings as a potential remedy for these shortcomings [27]. Lubrication at elevated temperatures is a critical aspect in numerous industrial sectors, such as aerospace, automotive, manufacturing, and military industries [28,46]. High-temperature lubricants possess unique properties that effectively mitigate friction and minimise wear between surfaces that are constantly rubbing against each other at high temperatures. Fig. 2.6 illustrates the stable working temperature range of several solid lubricants.

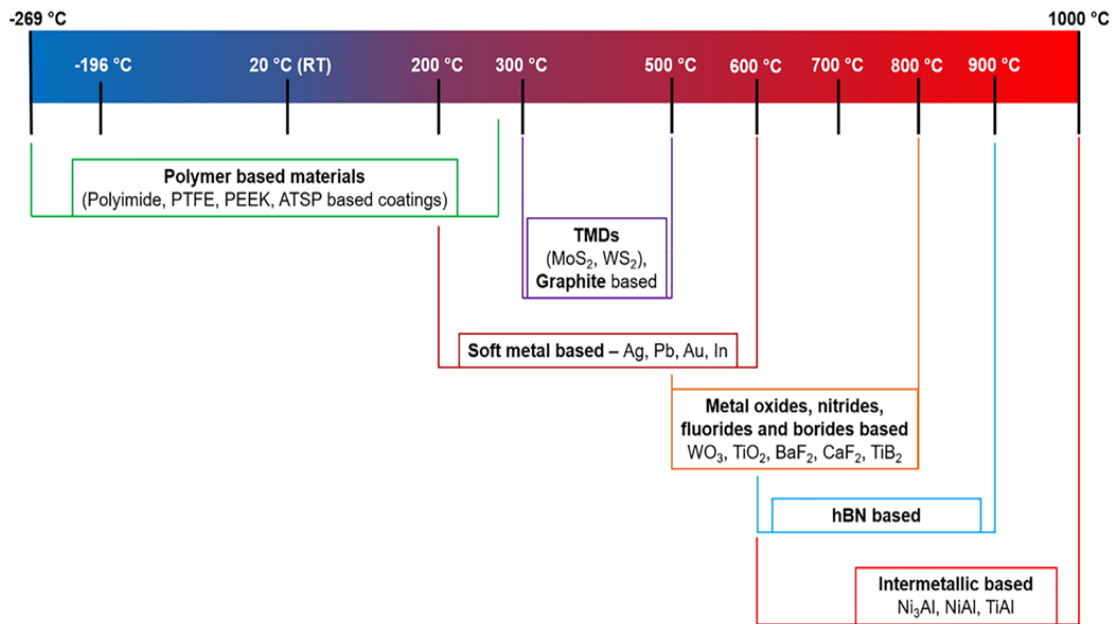


Fig. 2.6: The applicable working temperature range for different self-lubricating materials [28].

2.5 Architecture of high-temperature solid-lubricating materials

2.5.1 High-temperature matrix

Soft solid lubricants at high temperatures are unsuitable for bearing heavy loads and are prone to abrasive wear. Consequently, high-temperature materials must be utilized as the matrix to bind the solid lubricant and withstand the load. The high-temperature matrix material needs to be compatible with the solid lubricant in terms of its mechanical, physical, and chemical properties in order to have a low coefficient of friction and good wear resistance. In terms of mechanical properties, the high-temperature matrix material must possess favourable hardness, sufficient ductility, and high strength to withstand abrasive and fatigue wear. Additionally, high oxidation resistance is essential to prevent wear caused by oxidation at elevated temperatures. Moreover, having the appropriate thermal expansion coefficient is a critical factor for the formation of an effective lubricating film on the worn surface. High-temperature matrix materials typically fall into metals, intermetallic compounds, and ceramics. Furthermore, a reinforcing phase can be introduced into high-temperature matrix materials to enhance the hardness of metals and improve the toughness

of ceramics. In some cases, an assisting phase may be included to adjust the compatibility within the tribological system, taking into account factors such as thermal mismatch, corrosive properties, bonding strength, and transfer effects.

2.5.2 High-temperature solid lubricant

The term "high-temperature lubricant" refers to a class of lubricants (solid, liquid and gas) that may be utilised to minimise wear and friction between moving contact surfaces at high temperatures. 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 utilisation 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 common solid lubricants such as layered materials (WS_2 , graphite, MoS_2 , etc.), soft metals (Cu, Ag, Au, etc.), metal oxides (NiO, CuO, ZnO etc.), alkaline halides (CaF_2 , BaF_2 , etc.), double oxide phases (Ag_2MoO_4 , $Ag_2Mo_2O_7$, $BaMoO_4$, etc.) as well as MAX phases (Ti_3SiC_2 , Ti_2AlC , etc.) [47–49] have either been used or are being explored. It has been reported that Graphite and MoS_2 oxidise below 400 °C and cease to give lubrication beyond this temperature, whereas WS_2 continues to offer lubrication up to 500 °C [33,45,50]. Metal fluorides and oxides lubricate well at elevated temperatures but are ineffective at room temperature [51]. Silver offers lubrication up to 500 °C due to its superior thermal stability and ability to generate low-shearing stress junctions at the sliding interface [32,52,53]. The lamellar structure of hexagonal boron nitride (*h*BN), as well as its high thermal stability, good chemical inertness, high thermal conductivity, and white colour, makes it a promising candidate as a "clean" and high-temperature solid lubricant since it can maintain its lubricious & excellent adhesive characteristics over 500 °C [54,55]. However, poor

sintering and non-wetting features of *h*BN have restricted its applications, as reported by an earlier study [56]. A couple of recent studies have indicated an improvement in the sintering and wettability properties of *h*BN by modifying its surface with the help of Ni and Cu [57–59]. Also, it is well-established that a single lubricant fails to provide effective lubrication over a wide range of temperatures from room temperature (RT) to 800 °C or 1000 °C. Hence, addition of a combination of low and high-temperature solid lubricants is an effective way to realise the lubrication over a wide temperature range [29]. Silver (Ag) in conjunction with BaF₂/CaF₂ is a well-known solid lubricant combination. The soft metal Ag demonstrates solid lubrication properties at temperatures below 500 °C, while BaF₂/CaF₂ provides lubrication capabilities at temperatures exceeding 450 °C. The utilisation of Ag and BaF₂/CaF₂ in combination exhibits excellent lubricating properties across a wide temperature range, spanning from room temperature to 1000 °C. Apart from the traditional method of achieving lubrication by incorporating solid lubricants into a high-temperature matrix during the fabrication process, an alternative approach involves the in-situ formation of lubricious compounds through tribo-chemical reactions during friction. This design approach has been applied to various materials, including adaptive nitride-based high-temperature solid-lubricating coatings, nickel-based high-temperature solid-lubricating composites or coatings, and intermetallic-based high-temperature solid-lubricating composites, such as Ni₃Al, TiAl and NiAl [29]. Tables 2.1 and 2.2 lists the literature review on Ni-based high-temperature solid-lubricating coatings and composites.

Table 2.1: Review on Ni-based high-temperature solid-lubricating coatings

| Author (s), Journal (Year) | Synthesis technique and materials composition | Tested conditions/ Counterface | Results/Observations |
|---|--|--|--|
| Singh et al. [55,60] Surface & Coatings Technology (2023) | Atmospheric plasma spraying (APS) NiMoAl-Ag-WS ₂ /hBN | Ball on disc from 25 °C to 800 °C, sliding speed 0.35 m/s, load 5 N, sliding distance 630 m / Al ₂ O ₃ ceramic ball | Coatings exhibited low CoF (0.32-0.16, 0.30-0.15) and wear rate ($\sim 10^{-5}$ mm ³ /Nm) from 25 °C to 800 °C. Ag and WS ₂ provided lubrication from 25 °C to 400 °C. Silver molybdates, hBN, WO ₃ and MoO ₃ provided lubrication above 400 °C. |
| Dellacorte et al. [61,62] Tribology Transactions (1997, 2008) | Atmospheric plasma spraying (APS) NiCr-Cr ₂ O ₃ -20wt.% Ag-CaF ₂ /BaF ₂ | Pin on disc from 25 °C to 650 °C, sliding speed 1.0 m/s, load 4.9 N, sliding duration 60 min / Inconel 750 and Al ₂ O ₃ pins | Lower CoF and wear rate (0.23-0.31, 0.62-0.19; $3.9-6.6 \times 10^{-4}$ mm ³ /Nm, $2.3-0.78 \times 10^{-5}$ mm ³ /Nm) observed from RT to 650 °C against Inconel 750 and Al ₂ O ₃ and attributed to the combined lubricating effect of Ag and CaF ₂ /BaF ₂ . |
| Chen et al. [63] Tribology Letters (2014) | High velocity oxy fuel spraying (HVOF) NiMoAl-5wt.% Ag | Ball on disc from 20 °C to 800 °C, sliding speed 0.1 m/s, load 5 N, sliding distance 180 m / Si ₃ N ₄ ceramic ball | Coating exhibited lowest CoF (~ 0.3 from RT to 600 °C and 0.09 at 800 °C) and wear rate ($\sim 10^{-5}$ mm ³ /Nm at RT, 200 and 800 °C). Ag provided lubricity from RT to 400 °C. Ag ₂ Mo ₂ O ₇ and Ag ₂ MoO ₄ exhibited lubricity from 400 °C to 800 °C. |
| Tsigkis et al. [44] Tribology International (2021) | Atmospheric plasma spraying (APS) NiMoAl-Ag-CaF ₂ /BaF ₂ -Cr ₂ O ₃ | Pin on disc from 25 °C to 500 °C, sliding speed 0.16 m/s, load 5 N, sliding duration 25 min / 4130 steel, DLC, PCD and MoB/CoCr discs | PS400 vs. DLC showed lowest friction and wear from 25 °C to 500 °C. The DLC exhibited effective lubrication at 25 °C, while at 500 °C, oxide glazes were transferred onto the DLC surface, maintaining low friction. |

| | | | |
|---|---|--|--|
| Gautam et al. [64] Surface & Coatings Technology (2019) | Atmospheric plasma spraying (APS) Ni-Al-Ag-MoS ₂ -hBN | Ball on disc from RT to 800 °C, sliding speed 0.3 m/s, load 5 N, sliding distance 480 m / Al ₂ O ₃ ceramic ball | 5wt.% hBN addition exhibited lowest CoF and attributed to the synergetic action of Ag, MoS ₂ from RT to 400 °C and hBN in conjunction with lubricious molybdates beyond 600 °C. |
| Li et al. [65] J Alloy and compounds (2020) | Atmospheric plasma spraying (APS) on Inconel 718. NiCrAlY-20wt.% Ag-10wt.% Mo | Ball on disc from RT to 900 °C, sliding speed 0.19 m/s, load 5 N, sliding duration 30 min / Si ₃ N ₄ ceramic ball | Synergistic lubricating effect of Ag ₂ MoO ₄ , Ag ₂ Mo ₂ O ₇ , NiO and NiMoO ₄ effectively improved the tribological property of composite coating at high temperature. |
| Chen at al. [66] Surface & Coatings Technology (2014) | HVOF spraying NiMoAl-Cr ₃ C ₂ -10wt.% Ag | Ball on disc from 20 °C to 800 °C, rotating speed 600 rpm, load 15 N, sliding duration 45 min / Si ₃ N ₄ ceramic ball | Coatings exhibited improved friction and anti-wear properties (~ 0.3, 10 ⁻⁵ -10 ⁻⁶ mm ³ /Nm). Ag provided lubrication below 400 °C, whereas Ag ₂ MoO ₄ formed through tribo- chemistry provides lubrication at 600 °C and 800 °C. |
| Zhong et al. [67] Tribology International (2017) | APS spraying NiMoAl-6wt.% Al ₂ O ₃ -10wt.% Ag | Ball on disc from RT to 900 °C, sliding speed 0.1 m/s, load 12 N, sliding duration 30 min / Al ₂ O ₃ ceramic ball | At 900 °C, Coating exhibited lowest CoF (0.17) and wear rate (3.35 × 10 ⁻⁵ mm ³ /Nm) attributed to the Ag ₂ MoO ₄ based continous lubricating layer. |
| Chen et al. [68] Surface & Coatings Technology (2013) | APS spraying NiCrAlY-10wt.% Ag-10wt.% Mo | Ball on disc from 20 °C to 800 °C, sliding speed 0.3 m/s, load 5 N, sliding distance 200 m / Si ₃ N ₄ ceramic ball | Coatings exhibited low CoF (0.3) and wear rate (10 ⁻⁵ mm ³ /Nm) from RT to 800 °C. Ag provided lubrication below 400 °C. Ag ₂ MoO ₄ and MoO ₃ provides lubrication above 400 °C. |
| Zhang et al. [69] Surface & Coatings Technology (2017) | APS spraying NiCoCrAlY-Cr ₂ O ₃ -15wt.% (Ag- Mo) | Ball on disc from RT to 800 °C, sliding speed 0.2 m/s, load 10 N, sliding distance 240 m / Si ₃ N ₄ ceramic ball | Coatings showed lowest CoF and wear rate from RT to 800°C due to the synergetic lubricating effect of lubricious Ag, NiO, MoO ₃ , NiMoO ₄ and Ag ₂ MoO ₄ . |

| | | | |
|--|--|---|---|
| Li et al. [70] Tribology International (2017) | APS spraying NiAl-Cr ₂ O ₃ -Mo-Ag | Ball on disc from 25 °C to 900 °C, sliding speed 0.3 m/s, load 10 N, sliding time 60 min / Al ₂ O ₃ ceramic ball | Addition of Cr ₂ O ₃ improves anti wear properties. Formation of Ag, NiO, MoO ₃ , NiMoO ₄ , Ag ₂ MoO ₄ , Ag ₂ Mo ₄ O ₁₃ , Ag ₂ Mo ₂ O ₇ over the worn surfaces are responsible for improved tribological properties. |
| Xin et al. [71] Surface & Coatings Technology (2016) | Laser Cladding NiCrAlY- Cr ₃ C ₂ -(10, 20wt.%) V ₂ O ₅ -(10, 20wt.%) Ag ₂ O | Ball on disc from 25 °C to 800 °C, sliding speed 0.188 m/s, load 3 N, sliding time 45 min / Si ₃ N ₄ ceramic ball | Coating showed lowest CoF (0.147) and wear rate (2.86×10^{-5} mm ³ /Nm) at 800 °C, attributed to the synergetic action of carbides and silver vanadate (Ag ₃ VO ₄ and AgVO ₃) formed at elevated temperature. |
| Wang et al. [72] Optics and Laser Technology (2017) | Laser Cladding NiCrAlY-Cr ₃ C ₂ -20wt.% Ag- 10wt.% MoO ₃ . | Ball on disc from RT to 800 °C, rotating speed 360 rpm, load 3 N, sliding time 45 min / Si ₃ N ₄ ceramic ball | Coating showed the lowest CoF and wear rate at 600 °C and 800 °C and attributed to formation of glaze layer composed of Ag ₂ MoO ₄ . Ag provided lubrication at 200 °C, whereas MoO ₃ serve the purpose 400 °C. |
| Xin et al. [73] Surface & Coatings Technology (2017) | Laser Cladding NiCrAlY-Cr ₃ C ₂ (NiCr)-Cu/MoO ₃ | Ball on disc from 25 °C to 800 °C, sliding speed 0.19 m/s, load 3 N, sliding time 45 min / Si ₃ N ₄ ceramic ball | Synergistic lubricating effect of CuMoO ₄ , CuO, MoO ₃ , NiO and Cr ₂ O ₃ is responsible for reducing friction and wear of the composite coating at various temperatures. |

Table 2.2: Review of the tribological properties of Ni-based high-temperature solid-lubricating composites

| Author (s), Journal (Year) | Synthesis technique and materials composition | Tested conditions/ Counterface | Results/Observations |
|--|--|--|--|
| Ouyang et al. [74] Wear (2015) | Hot pressing sintering NiCr-(10,20wt.%) BaMoO ₄ | Ball on disc from RT to 600 °C, rotating speed 400 rpm, load 5 N, sliding time 60 min / Si ₃ N ₄ ceramic ball | NiCr-BaMoO ₄ composites exhibited lower CoF (0.26-0.30) and wear rate (10 ⁻⁵ -10 ⁻⁶ mm ³ /Nm) at elevated temperatures due to combined action of BaMoO ₄ , NiCr ₂ O ₄ , NiO and Cr ₂ O ₃ . |
| Ouyang et al. [75] Wear (2013) | Hot pressing sintering NiCr-(10-30wt.%) BaCr ₂ O ₄ | Ball on disc from RT to 800 °C, rotating speed 400 rpm, load 5 N, sliding time 60 min / Si ₃ N ₄ ceramic ball | NiCr-20BaCr ₂ O ₄ composite exhibits lower CoF (0.27) and wear rate (4.5-10 ⁻⁶ mm ³ /Nm) and attributed these to protective oxide glaze layer composed of BaCr ₂ O ₄ and BaCrO ₄ . |
| Feng et al. [76] Journal of Wuhan University of Technology-Mater. Sci. Ed. (2019) | Spark plasma sintering NiCr-10wt.% Ti ₃ SiC ₂ -(3-10wt.%) Ag ₂ W ₂ O ₇ | Ball on disc from 20 °C to 600 °C, sliding speed 0.2 m/s, load 10 N, sliding time 60 min / Si ₃ N ₄ ceramic ball | Composite with 20wt.% Ti ₃ SiC ₂ -5wt.% Ag ₂ W ₂ O ₇ exhibits better tribological properties (0.33-0.49, 7.07-9.89×10 ⁻⁵ mm ³ /Nm) over a wide temperature range and attributed these to the synergistic effects of Ag and lubricious mixture of Ni, Ti, Si and W oxides. |
| Li et al. [53] Tribology Letters (2013) | Hot pressing sintering NiCrMoAl-12wt.% Ag-10wt.% CaF ₂ /BaF ₂ | Pin on disc from 25 °C to 800 °C, sliding speed 1.0 m/s, load 10 N, sliding time 20 min / Inconel 718 Pin | Composite exhibited lower friction (0.25) from 25 °C to 800 °C and ascribed to supportive lubricant effect of Ag and CaF ₂ /BaF ₂ . |
| Zhen et al. [77] Tribology International (2014) | Hot pressing sintering NiCrMoTiAl-12.5 wt.% Ag-(5-15wt.%) CaF ₂ /BaF ₂ | Ball on disc from RT to 900 °C, sliding speed 1.0 m/s, load 5 N, sliding time 30 min / Si ₃ N ₄ ceramic ball | Composites exhibited lower CoF (0.23-0.31) and wear rate (1.1-43×10 ⁻⁵ mm ³ /Nm) from RT to 900 °C and attributed these to synergetic lubricating action of Ag and CaF ₂ /BaF ₂ . |

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|--|--|--|--|
| Zhen et al. [78] Tribology International (2017) | Hot pressing sintering NiCrMoTiAl-Ag-MoS ₂ -CaF ₂ | Ball on disc from 25 °C to 700 °C, sliding speed 1.0 m/s, load 5 N, sliding time 30 min / Si ₃ N ₄ ceramic ball | Composites exhibited low CoF (0.16-0.40) and wear rate ($1-29.4 \times 10^{-5}$ mm ³ / Nm) and attributed these to the synergistic effect of Ag, MoS ₂ , CaF ₂ , MoO ₃ and Cr _x S _y . |
| Zhen et al. [79] Tribology International (2017) | Hot pressing sintering NiCrMoTiAl-12.5wt.% Ag-5wt.% CaF ₂ /BaF ₂ | Ball on disc from RT to 800 °C in Air and Vacuum environment, sliding speed 0.8 m/s, load 5 N, sliding time 30 min / Si ₃ N ₄ ceramic ball | Composites exhibited better performance under vacuum conditions below 600 °C due to the formation of stable Ag film. At 800 °C, composites performed better in air environment due to the presence of a compacted glazed layer composed mainly of MoO ₃ , NiO, BaTiO ₃ , BaMoO ₄ and NiCr ₂ O ₄ . |
| Cheng et al. [80] Materials and Design (2017) | Hot pressing sintering NiCrMoAl-12.5wt.% Ag-(5-10wt.%) CaF ₂ /BaF ₂ | Ball on disc from RT to 800 °C in vacuum environment, sliding speed 0.785 m/s, load 5 N, sliding time 80 min / Si ₃ N ₄ ceramic ball | Ag provided the lubricating effect below 400 °C. BaF ₂ /CaF ₂ provided the lubrication effect from 400 °C to 800 °C. |
| Liu et al. [81] Tribology Transactions (2013) | Hot pressing sintering NiMoAl-Cr ₂ O ₃ -(10-20wt.%) Ag ₂ Mo ₂ O ₇ | Pin on disc from RT to 800 °C, sliding speed 0.287 m/s, load 2 N, sliding time 60 min / Inconel 718 disc | Composite with 20 wt.% Ag ₂ Mo ₂ O ₇ exhibited lower CoF (0.3) and wear rate (1.51×10^{-5} mm ³ /Nm) and ascribed these to synergistic lubricating effect MoO ₃ , Ag ₂ Mo ₂ O ₇ and iron oxide (Fe ₂ O ₃ and Fe ₃ O ₄). |
| Liu et al. [82] Tribology Letters (2012) | Hot pressing sintering NiMoAl-Cr ₂ O ₃ -(10, 20wt.%) Ag ₂ MoO ₄ | Pin on disc from RT to 700 °C, sliding speed 0.287 m/s, load 2 N, sliding time 60 min / Inconel 718 disc | Composite with 20 wt.% Ag ₂ MoO ₄ exhibited lower CoF (0.26) and wear rate (1.02×10^{-5} mm ³ /Nm) at 700 °C and attributed these to synergistic lubricating effect of Ag ₂ MoO ₄ and iron oxide at elevated temperatures. |
| Tyagi et al. [56] Wear (2010) | Hot pressing sintering NiCrWMoAlTi-8wt.% hBN-(8, 12, 16 and 20wt.%) nano Ag | Ring on disc from RT to 600 °C, sliding speed 1.0 m/s, load 20 N, sliding distance 625 m / AISI52100 steel ring | Composites containing Ag-hBN exhibited lowest CoF and ascribed to the presence of Ag and hBN on the worn surface of the composites. |

2.6 Intermetallic (Ni₃Al and NiAl) based high-temperature solid-lubricating composites

Intermetallic compounds possess a combination of ceramic and metallic properties due to their strong internal order and mixed bonding (metallic and covalent or ionic). These compounds are particularly valuable when hardness and/or resistance to high temperatures are prioritised over toughness and ease of processing [83]. In recent times, there has been a surge in research on intermetallic matrix materials, resulting in the development of several innovative high-temperature solid-lubricating materials. These include nickel aluminium matrix [25,34,35,84,85], titanium aluminium matrix [52,86], ferric aluminium matrix [87], nickel silicon matrix and other high-temperature solid-lubricating materials [88,89].

Ni₃Al-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 [90–92], which make these 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 [93–95]. The inherent brittle nature of intermetallic compounds at room as well as elevated temperatures affects their tribological performance in an adverse manner and restricts their use in components having relative motion while in contact with their mating counterpart [96–98]. It has been indicated that friction and wear performance of Ni₃Al intermetallic compounds can be improved by integrating alloying elements, other reinforced phases, solid lubricants and regulating the reaction sintering process [99–101]. A recent development involved the synthesis of Ni₃Al matrix high-temperature solid-lubricating composites [25,29,34,35,42,100–106]. Solid-lubricating composites comprising a Ni₃Al matrix, solid lubricants (such as graphite, MoS₂, hBN, Ag, Au, fluorides, inorganic salts, etc.), and reinforcements (Cr, Mo, W, TiC, Al₂O₃, Cr₂O₃, Cr₃C₂, etc.), demonstrate favourable tribological properties in terms of low friction coefficient ($\mu < 0.35$) and wear rate ($\sim 10^{-4}$ to 10^{-5} mm³/Nm) across a broad temperature range spanning from room temperature to 1000 °C. Table 2.3 lists the tribological characteristics of intermetallic (Ni₃Al and NiAl) matrix solid-lubricating composites and coatings.

Table 2.3: Review of the tribological properties of intermetallic (Ni₃Al and NiAl) matrix solid-lubricating composites or coatings.

| Ni₃Al matrix solid-lubricating composites or coatings | | | |
|--|--|--|---|
| Author (s), Journal (Year) Matrix | Synthesis technique and Lubricants | Tested conditions/ Counterface | Results/Observations |
| Zhai et al. [34] Tribology Transactions (2015) Matrix: Ni ₃ Al | <ul style="list-style-type: none"> High energy ball milling (10 h, 200 rpm) followed by spark plasma sintering at 1150 °C (35 MPa, 12 min) in pure Ar atmosphere. Lubricants: WS₂-Ti₃SiC₂ (5-15wt.%) | Ball on disc from RT to 800 °C, sliding speed 0.2 m/s, load 10 N, sliding time 80 min / Si ₃ N ₄ ceramic ball | <ul style="list-style-type: none"> Ni₃Al-10wt.% of WS₂-Ti₃SiC₂ exhibited the lowest CoF ($\mu \sim 0.18-0.31$) and wear rate ($W \sim 1.5-3.1 \times 10^{-5} \text{ mm}^3/\text{Nm}$) from RT to 800 °C. WS₂ provided lubricity from RT to 400 °C and Ti₃SiC₂ exhibited lubricity from 400 to 800 °C. |
| Shi et al. [35] Materials and design (2014) Matrix: Ni ₃ Al | <ul style="list-style-type: none"> High energy ball milling (10 h, 200 rpm) followed by spark plasma sintering at 1150 °C (30 MPa, 6 min) in pure Ar Lubricants: WS₂-Ag-hBN (10, 15 and 20 wt.%) | Ball on disc from 30 °C to 800 °C, sliding speed 0.234 m/s, load 10 N, sliding time 80 min / Si ₃ N ₄ ceramic ball | <ul style="list-style-type: none"> At 600 °C, the lowest friction ($\mu \sim 0.25$) and wear ($W \sim 0.9 \times 10^{-4} \text{ mm}^3/\text{Nm}$) were reported for Ni₃Al-15wt.% of WS₂-Ag-hBN. Ag and WS₂ provided self-lubrication at low temperature, whereas hBN at elevated temperatures. |
| Zhu et al. [102] Tribology International (2011) Matrix: Ni ₃ Al | <ul style="list-style-type: none"> High energy ball milling (8 h, 300 rpm) followed by vacuum hot press sintering at 900 °C (15 min, 35 MPa) powders again heated to 1100 °C for 20 min. Lubricants: Cr-Ag-CaF₂/BaF₂ 10-25 wt.% of Cr | Ball on disc from RT to 1000 °C, sliding speed 0.19 m/s, load 20 N, sliding time 60 min / Si ₃ N ₄ ceramic ball | <ul style="list-style-type: none"> Lowest CoF ($\mu \sim 0.24-0.37$) and wear rate ($W \sim 0.52-2.32 \times 10^{-4} \text{ mm}^3/\text{Nm}$) observed for Ni₃Al-Ag-CaF₂/BaF₂-20wt.% Cr over broad temperature range. At 800 °C, the lowest CoF (0.24) and wear rate ($0.71 \times 10^{-4} \text{ mm}^3/\text{Nm}$) was observed. 20 wt. % Cr addition is recommended for excellent lubricity. |
| Zhu et al. [106] Tribology International (2011) Matrix: Ni ₃ Al | <ul style="list-style-type: none"> High energy ball milling (8 h, 300 rpm) followed by vacuum hot press sintering at 900 °C (15 min, 35 MPa) powders again heated to 1100 °C for 20 min. | Ball on disc from 20 °C to 800 °C, sliding speed 0.188 m/s, load 10 N, sliding time 60 min / Si ₃ N ₄ ceramic ball | <ul style="list-style-type: none"> Low CoF ($\mu \sim 0.30-0.36$) and wear rate ($W \sim 0.65-2.45 \times 10^{-4} \text{ mm}^3/\text{Nm}$) observed from RT to 800 °C. The supportive lubricating action of Ag, BaF₂/CaF₂ and BaCrO₄/CaCrO₄ observed from |

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|---|---|---|--|
| | <ul style="list-style-type: none"> • Lubricants: Cr-Ag-CaF₂/BaF₂ • 10-25 wt.% of Cr | | RT to 800 °C |
| Yan et al. [107] JMEPEG (2017) Matrix: Ni ₃ Al | <ul style="list-style-type: none"> • High energy ball milling (8 h, 300 rpm) followed by vacuum hot press sintering at 700 °C and held for 15 min under 70 MPa until heated to 900 °C and then heated to 1100 °C and held for 15 min. • Lubricants: Mo-Ag-CaF₂/BaF₂ | Ball on disc from 20 °C to 1000 °C, sliding speed 0.2 m/s, load 20 N, sliding duration 30 min / Si ₃ N ₄ , SiC and Al ₂ O ₃ ceramic balls | <ul style="list-style-type: none"> • Ni₃Al-Cr-Ag-CaF₂/BaF₂ composite against Si₃N₄ possessed low CoF ($\mu \sim 0.31$) and wear rate ($W \sim 0.52-2.25 \times 10^{-4} \text{ mm}^3/\text{Nm}$) from RT to 1000 °C. • The synergistic lubricating effect of Ag, BaF₂/CaF₂ and Molybdates observed from RT to 1000 °C. |
| Niu et al. [105] Surface & Coatings Technology (2012) Matrix: Ni ₃ Al | <ul style="list-style-type: none"> • Ball milling (8 h) followed by vacuum hot press sintering at 1100 °C (30 MPa, 30 min) • Lubricants: Ag-Mo and BaF₂/CaF₂ | Ball on disc from 25 °C to 1000 °C, sliding speed 0.2 m/s, load 20 N, sliding duration 20 min / Si ₃ N ₄ ceramic ball | <ul style="list-style-type: none"> • Low CoF over RT to 1000 °C • Ag provides a lubricating effect below 400 °C • BaF₂/CaF₂ provided the lubrication effect from 400 to 800 °C • Molybdates provide superior lubrication above 800 °C |
| Zhu et al. [100] Tribology Letters (2012) Matrix: Ni ₃ Al | <ul style="list-style-type: none"> • Vacuum arc melting and casting. • Lubricants: W-Ag-CaF₂/BaF₂ • 10, 15 and 20 wt.% of BaF₂/CaF₂ | Ball on disc from RT to 800 °C, sliding speed 0.19 m/s, load 10 N, testing time 60 min / Si ₃ N ₄ ceramic ball | <ul style="list-style-type: none"> • Ni₃Al-W-Ag-15wt.% CaF₂/BaF₂ composite exhibited low CoF ($\mu \sim 0.31-0.4$) and wear rate ($W \sim 0.2-6.2 \times 10^{-4} \text{ mm}^3/\text{Nm}$) from RT to 800 °C. • The supportive lubricant effect of Ag, CaF₂/BaF₂, BaWO₄ and CaWO₄ observed between RT and 800 °C. |
| Zhu et al. [104] Tribology International (2015) Matrix: Ni ₃ Al | <ul style="list-style-type: none"> • Ball milling followed by hot press sintering at 1100 °C (15 min, 35 MPa) powders again heated to 1200 °C for 20 min. • Lubricants: Ag, BaCrO₄ and BaMoO₄. | Ball on disc at 20 °C to 800 °C, speed 0.19 m/s, load 20 N, sliding time 30 min / Si ₃ N ₄ ceramic ball. | <ul style="list-style-type: none"> • The CoF observed from 0.29 to 0.38 and 0.28-35 from RT to 800°C for Ag-BaCrO₄ and Ag-BaMoO₄ combinations. • The low CoF is because of the combined lubricating effect of Ag, BaCrO₄ and BaMoO₄. |

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| Wang et al. [25] Tribology International (2021) Matrix: Ni ₃ Al | <ul style="list-style-type: none"> • High-energy ball milling (8 h) followed by vacuum hot press sintering at 900 °C (15 min, 35 MPa) powders again heated to 1100 °C for 20 min. • Lubricant: Ag (10 and 20 wt.%) | Ball on disc from RT to 900 °C, speed 0.2 m/s, load 10 N, sliding time 30 min / Si ₃ N ₄ ceramic ball | <ul style="list-style-type: none"> • Ag provides lubricity between RT to 400 °C • Ag₂MoO₄ and NiO provides lubricity between 800 °C and 900 °C. • Silver film and oxide layers impart a synergistic effect that provides continuous lubricity over a broad range of temperatures. |
| Zhang et al. [103] Journal of Alloys and Compounds (2009) Matrix: Ni ₃ Al | <ul style="list-style-type: none"> • Cold compaction (600 MPa) followed by vacuum hot press sintering at 700 °C (30 min, 30 MPa) and diffusion annealed at 1080 °C for 240 min. • Lubricants: Ag-hBN | Ball on disc from RT to 800 °C, speed 0.132 m/s, load 5 N, sliding duration 20 min / Si ₃ N ₄ ceramic ball | <ul style="list-style-type: none"> • Low CoF ($\mu \sim 0.32-0.48$) and wear rate ($W \sim 2.3-5.2 \times 10^{-5} \text{ mm}^3/\text{Nm}$) observed from RT to 800 °C. • Ag provided a lubricating effect between RT to 400 °C • hBN provided the lubrication effect beyond 500°C |
| Shi et al. [101] Wear (2013) Matrix: Ni ₃ Al | <ul style="list-style-type: none"> • High-energy ball milling (12 h, 200 rpm) followed by spark plasma sintering at 1150 °C (30 MPa, 6 min) in pure Ar environment • Lubricant: 15 wt.% Ti₃SiC₂ | Ball on disc from 25 °C to 800 °C, speed 0.2 m/s, load 10 N, sliding duration 80 min / Si ₃ N ₄ , Al ₂ O ₃ and WC-6Co balls | <ul style="list-style-type: none"> • They reported CoF and wear rate in the range of 0.44-0.51 and $0.64-4.2 \times 10^{-5} \text{ mm}^3/\text{Nm}$ against Al₂O₃, 0.41-0.50 and $2.8-3.7 \times 10^{-5} \text{ mm}^3/\text{Nm}$ against WC-6Co, and 0.31-0.48 and $0.34-2.1 \times 10^{-5} \text{ mm}^3/\text{Nm}$ against Si₃N₄ from 25 to 800 °C. |
| Yan et al. [42] JMEPEG (2017) Matrix: Ni ₃ Al | <ul style="list-style-type: none"> • Vibratory ball milling (10 h, 45 Hz) followed by spark plasma sintering at 1100 °C (40 MPa, 5 min) in pure Ar environment • Lubricants: 1.5 wt.% MLG-10 wt.% Ti₃SiC₂ | Ball on disc from RT to 750 °C, speed 0.2 m/s, load 12 N, sliding time 80 min / Si ₃ N ₄ ball | <ul style="list-style-type: none"> • They reported lower CoF (0.26-0.57) and wear rate ($3.1-6.5 \times 10^{-5} \text{ mm}^3/\text{Nm}$) over a wide range of temperatures and attributed these to the synergetic lubricating action of MLG and Ti₃SiC₂. |
| Wang et al. [108] Wear (2021) Matrix: Ni ₃ Al-Ni ₃ Nb | <ul style="list-style-type: none"> • High-energy ball milling (8 h, 250 rpm) followed by vacuum hot press sintering at 900 °C (15 min, 35 MPa) and again heated to 1000 °C for 20 min. • Lubricant: 20 wt.% Ag | Ball on disc from RT to 900 °C, speed 0.188 m/s, load 10 N, sliding duration 30 min / Si ₃ N ₄ ball | <ul style="list-style-type: none"> • Ni₃Al-Ni₃Nb-Ag (20:60:20 wt.%) composite showed lower CoF (0.39-0.31) and wear rate ($1.05-4.68 \times 10^{-5} \text{ mm}^3/\text{Nm}$) from RT to 900 °C. • Synergistic effects of low-moderate temperature solid lubricant (Ag) and high temperature solid lubricant (AgNbO₃) played a significant role in |

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| | <ul style="list-style-type: none"> 60:20:20 wt.% and 20:60:20 wt.% | | lubrication over a wide temperature range. |
| Huang et al. [109] JMEPEG (2017) Matrix: Ni ₃ Al | <ul style="list-style-type: none"> Vibratory ball milling followed by spark plasm sintering at 1150 °C (35 MPa, 5 min) in pure Ar environment. Lubricants: 10 wt.% Ag and 1.5 wt.% MoO₃. | Ball on disc from 20 °C to 800 °C, speed 0.2 m/s, load 4, 8, 12 and 16 N, testing time 80 min / Si ₃ N ₄ ball | <ul style="list-style-type: none"> They reported a thick friction layer (5 μm) at 12 N and 400 °C compared to other loading and temperature condition. The friction layer avoids the generation of cracks and the spalling of subsurface materials during the dry sliding process. |
| Yao et al. [110] JMEPEG (2015) Matrix: Ni ₃ Al | <ul style="list-style-type: none"> High energy ball milling (12 h, 200 rpm) followed by spark plasm sintering at 1100 °C (40 MPa, 5 min) in pure Ar atmosphere. Lubricants: 15 wt.% (Ag-Ti₃SiC₂), 15 wt.% (MoS₂-Ti₃SiC₂) and 15 wt.% (WS₂-ZnO) | Ball on disc from 25 °C to 800 °C, speed 0.2 m/s, load 10 N, sliding time 80 min / Si ₃ N ₄ ball | <ul style="list-style-type: none"> MoS₂-Ti₃SiC₂ solid lubricant combination showed lower CoF (0.26-0.32) and wear rate (0.8-2.1 × 10⁻⁵ mm³/Nm) MoS₂ played a dominant role in self-lubrication in low temperature regime (< 400 °C). Ti₃SiC₂ provided superior self-lubrication at high temperature. |
| Zhai et al. [111] JMEPEG (2014) Matrix: Ni ₃ Al | <ul style="list-style-type: none"> High energy ball milling (10 h, 200 rpm) followed by spark plasm sintering at 1150 °C (40 MPa, 5 min) in pure Ar atmosphere. Lubricant: Ti₃SiC₂ (5, 10, 15 and 20 wt.%) | Ball on disc from 25 °C to 800 °C, speed 0.2 m/s, load 10 N, sliding time 20 min / Si ₃ N ₄ ball | <ul style="list-style-type: none"> Ni₃Al-15wt.% Ti₃SiC₂ composite has been reported to maintain a low CoF (0.17-0.58) and wear rate (0.31-4.2 × 10⁻⁵ mm³/Nm) from 25 °C to 800 °C. Ti₃SiC₂ oxidation reaction forms tribo layer on the worn surface at 800 °C, which provides superior lubrication. |
| Zhu et al. [112] Tribology Letters (2011) Matrix: Ni ₃ Al | <ul style="list-style-type: none"> High-energy ball milling (8 h) followed by hot press sintering at 1200 °C (20 min, 35 MPa). Lubricant: BaMoO₄ (10, 15 and 20 wt.%) | Ball on disc from 20 °C to 800 °C, speed 0.188 m/s, load 20 N, sliding duration 60 min / Si ₃ N ₄ ball | <ul style="list-style-type: none"> Ni₃Al-15 wt.% BaMoO₄ composite had shown a lowest CoF (~ 0.26) and wear rate (~ 1.10 × 10⁻⁵ mm³/Nm) at 600 °C and attributed these to the lubricating capability of BaMoO₄ at higher temperatures. |

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| <p>Liu et al. [113] Materials Research Express (2018)</p> <p>Matrix: Ni₃Al</p> | <ul style="list-style-type: none"> • Spark plasma sintering (SPS, 1100 °C, 40 MPa, 5 min and Ar atmosphere) • Laser melting deposition (LMD, CO₂ laser, 1800 W) • Lubricants: 10 wt.% Ag-1.5 wt.% MLG | <p>Ball on disc from 25 °C to 500 °C, speed 0.2 m/s, load 12 N, sliding duration 60 min / Si₃N₄ ball</p> | <ul style="list-style-type: none"> • They reported a lower CoF (0.20-0.40) and wear rates ($2.8-5.0 \times 10^{-5}$ mm³/Nm) for LMD composite compared to SPS composite from 25 to 500 °C and attributed these to the increased hardness as well as synergetic lubricating effect of Ag and MLG. |
| <p>Zhu et al. [114] Journal of Tribology (2019)</p> <p>Matrix: Ni₃Al</p> | <ul style="list-style-type: none"> • High-energy ball milling (8 h) followed by hot press sintering at 1100 °C (20 min, 35 MPa). • Lubricants: Ag (12.5 wt.%) and V₂O₅ (2 and 5 wt.%) | <p>Ball on disc from 20 °C to 1000 °C, speed 0.2 m/s, load 10 N, sliding duration 30 min / Si₃N₄ ball</p> | <ul style="list-style-type: none"> • Ni₃Al-2V₂O₅-12.5Ag composite showed lower CoF (0.25-0.4) and wear rate (10^{-5} mm³/Nm) from 20 °C to 1000 °C and attributed these to the synergistic action of Ag and Ag₃VO₄ formed at high temperatures by tribo-chemistry. |
| <p>Zhai et al. [115] Wear (2014)</p> <p>Matrix: Ni₃Al</p> | <ul style="list-style-type: none"> • Ball milling (6 h, 120 rpm) followed by spark plasma sintering at 1150 °C (30 MPa, 6 min) in pure Argon • Lubricant: Graphene nanoplatelets (GNPs, 1 wt.%) | <p>Ball on disc from 25 °C to 600 °C, speed 0.2 m/s, load 10 N, sliding duration 30 min / Si₃N₄ ball</p> | <ul style="list-style-type: none"> • Low CoF ($\mu \sim 0.21-0.26$) and wear rate ($4.1-5.3 \times 10^{-6}$ mm³/Nm) over RT to 400 °C. • GNPs provides a lubrication effect below 400 °C. • Wear mechanism: Refinement of grains and the slippage of laminated sheets between GNPs. |
| <p>Fan et al. [116] Surface & Coatings Technology (2023)</p> <p>Matrix: Ni₃Al</p> | <ul style="list-style-type: none"> • Ball milling (4 h) followed by high velocity oxygen fuel spraying (HVOF) on AISI 310 Stainless Steel. • Lubricants: Ag-MoO₃ • Hardener: Cr₃C₂ (0,10,15 and 20 wt.%) | <p>Ball on disc from 25 °C to 600 °C, speed 0.19 m/s, load 5 N, sliding duration 30 min / Si₃N₄ ball</p> | <ul style="list-style-type: none"> • Ni₃Al-Ag-MoO₃-15 wt.% Cr₃C₂ coatings exhibited lower CoF (0.60-0.26) and wear rate ($14.48-2.01 \times 10^{-5}$ mm³/Nm) and attributed these to the synergistic lubrication effect of Ag, MoO₃, NiCr₂O₄ and Ag₂MoO₄. |
| <p>Fan et al. [117] Coatings (2023)</p> <p>Matrix: Ni₃Al</p> | <ul style="list-style-type: none"> • Ball milling (3 h) followed by HVOF spraying on AISI 310 Stainless Steel. • Lubricants: 10 wt.% Ag and MoO₃ (10, 15 and 20 wt.%) | <p>Ball on disc from 25 °C to 800 °C, speed 0.19 m/s, load 5 N, sliding duration 30 min / Si₃N₄ ball</p> | <ul style="list-style-type: none"> • Low CoF (0.63-0.36) and wear rate ($25.11-6.03 \times 10^{-5}$ mm³/Nm) reported for Ni₃Al-Ag-15 wt.% MoO₃ coatings from 25 to 800 °C and ascribed these to the supportive lubricating action of NiO, Al₂O₃, MoO₃ and Ag₂MoO₄. |

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| Huang et al. [118] Coatings (2023) Matrix: Ni ₃ Al | <ul style="list-style-type: none"> Ball milling followed by laser melting deposition (LMD) Lubricants: 10 wt.% (Sn-Ag-Cu) and 12 wt.% Ti₃SiC₂ | Ball on disc from 20 °C to 800 °C, speed 0.2 m/s, load 12 N, sliding duration 60 min / Si ₃ N ₄ ball | <ul style="list-style-type: none"> Low CoF (0.22-0.29) and wear rate (0.65-1.25 × 10⁻⁵ mm³/Nm) observed from 20 °C to 800 °C. Ag, Al₂O₃, SnO₂ and CuO provided lubrication from 20 °C to 400 °C, whereas Al₂O₃, TiO₂ and SiO₂ provided lubrication from 600 °C to 800 °C. |
| Fan et al. [119] Journal of Thermal Spray and Technology (2022) | Self-propagating high temperature synthesis followed by HVOF spraying on AISI 310 Stainless Steel. | Ball on disc from 25 °C to 800 °C, speed 0.19 m/s, load 5 N, sliding duration 30 min / Si ₃ N ₄ ball | <ul style="list-style-type: none"> At 600 °C, the coating showed the lowest CoF ($\mu \sim 0.57$) and wear rate ($W \sim 8.91 \times 10^{-5}$ mm³/Nm) and attributed these to the synergistic lubrication effect of NiO, Ni₂O₃, Al₂O₃ and NiAl₂O₄. |
| Solmaz et al. [120] Wear (2004) | Hot rolling of Boron-doped Ni ₃ Al sheet material. | Block on disc from 25 °C to 450 °C, speed 1 m/s, load 50, 75, 100 and 125 N, sliding duration 20 min / 100Cr6 steel disc | <ul style="list-style-type: none"> Weight loss peaks at 100 °C for all loads, then drops below 25 °C due to a thinner, easily removable oxide layer on the worn surface. Dominant wear mechanism: oxidational wear. |
| Room Temperature, Ni₃Al matrix solid-lubricating composites or coatings | | | |
| Wang et al. [121] Applied surface science (2022) Matrix: Ni ₃ Al | <ul style="list-style-type: none"> Electrohydrodynamic atomization (EHDA) Lubricants: Ti₃SiC₂-MoS₂ Substrate: GH3044 superalloy | Ball on disc at RT, speed 6 mm/s, load 5 N, testing time 20 min / Si ₃ N ₄ ball | <ul style="list-style-type: none"> Triple layer micro-laminated films showed superior cohesion, adhesion and tribological performance compared to single and double layer micro-laminated films due to its micro-laminated structure inhibiting crack propagation and reduces film damage. |
| Wang et al. [122] Wear (2022) Matrix: Ni ₃ Al | <ul style="list-style-type: none"> Laser surface texturing (LST) followed by EHDA Lubricants: 5 wt.% MoS₂ and Ti₃SiC₂ (3, 5 and 8 wt.%) Substrate: GH3044 superalloy | Ball on disc at 25 °C, frequency 6 Hz, load 5 N, sliding time 15 min / Si ₃ N ₄ ball | <ul style="list-style-type: none"> Ni₃Al-MoS₂-8wt.%Ti₃SiC₂ composite coating reported lowest CoF (0.25) and wear rate (2.259×10⁻⁵ mm³/Nm) and attributed these to the synergistic lubricating function of MoS₂ and Ti₃SiC₂. |
| Song et al. [97] Material and Design (2019) | <ul style="list-style-type: none"> Selective laser melting Lubricant: Boron nitride nanoplatelet (BNNP) (10, 15 and 20 wt.%) | Ball on disc at RT, speed 0.28 m/s, load 3 and 9 N, sliding distance 500 m / Si ₃ N ₄ ceramic ball | <ul style="list-style-type: none"> Composite had shown a lowest CoF (0.22-0.26) and wear rate (0.9-2.1 × 10⁻⁵ mm³/Nm) and attributed these to the synergetic strengthening / toughening and lubricating capability of BNNP. |

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| Matrix: Ni ₃ Al | | | |
| Wang et al. [123] Vacuum (2022) Matrix: Ni ₃ Al | <ul style="list-style-type: none"> • EHDA • Monomer film: Ni₃Al, Micro-laminate composite films: Ni₃Al–Cr₃C₂/Ni₃Al • Substrate: SS 316 | Ball on disc at 25 °C, speed 10 mm/s, stroke length 6 mm, load 10 N, sliding time 20 min / Si ₃ N ₄ ball | <ul style="list-style-type: none"> • Enhanced mechanical and tribological properties observed for micro-laminate composite films compared to monomer film. • Wear mechanism: Ni₃Al: Adhesion and Abrasion; Ni₃Al–Cr₃C₂/Ni₃Al: Abrasion |
| Huang et al. [124] Material Research Express (2022) Matrix: Ni ₃ Al | <ul style="list-style-type: none"> • Laser melt deposition (LMD) • Ni₃Al-gradient composite structure (GCS) • GCS: Sn-Ag-Cu and Ti₃SiC₂ | Ball on disc at 25 °C, speed 0.2 m/s, load 4-16 N, sliding duration 90 min / GCr15 steel balls | <ul style="list-style-type: none"> • At 12 N, Ni₃Al-GCS composites have shown improved tribological characteristics (~ 0.23, 3.5 μm and 5.3 × 10⁻⁶ mm³/Nm) due to the formation of friction interface layer rich in the lubrication phase and oxides. |
| Lu et al. [41] Wear (2019) Matrix: Ni ₃ Al | <ul style="list-style-type: none"> • Ball milling (6h, 120 rpm) followed by Laser melt deposition (LMD) • Lubricant: GNPs | Ball on disc at RT, speed 0.2 m/s, load 5 N-30 N, distance 1000 m / Si ₃ N ₄ ball | <ul style="list-style-type: none"> • At 20 N, Ni₃Al-GNPs exhibited stable CoF and low wear rate due to the formation of tribo-layer containing lubricious oxides and GNPs. |
| NiAl matrix solid-lubricating composites | | | |
| Zhu et al. [125] Wear (2012) | Hot press sintering NiAl-Cr-Mo-15wt. % of ZnO/CuO | Ball on disc from 20 °C to 1000 °C, speed 0.19 m/s, load 10 N / Si ₃ N ₄ ball | <ul style="list-style-type: none"> • At 800 °C and 1000 °C, composites with addition of ZnO/CuO showed the better self-lubricating performance. • Attributed to the formation of ZnO/CuO layer on the worn surface. |

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| Zhu et al. [126] Journal of Tribology (2016) | Hot press sintering NiAl-Cr-Mo-CuO (15-30 wt.% CuO) | Ball on disc from 20 °C to 1000 °C, speed 0.19 m/s, load 10 N / Si ₃ N ₄ ball | <ul style="list-style-type: none"> Composite with 25 wt.% CuO had a favorable friction coefficient (0.2) and excellent wear resistance (10⁻⁶mm³/Nm) at 800 and 1000 °C and attributed these to the formation of a glaze layer consisting mainly of CuO and MoO₃ on the worn surface. |
| Zhu et al. [127] Tribology letters (2011) | Hot press sintering NiAl-Cr-Mo-CaF ₂ | Ball on disc from 20 °C to 1000 °C, speed 0.188 m/s, load 10 N / Si ₃ N ₄ ball | <ul style="list-style-type: none"> At 800 °C and 1000 °C, composite provides an excellent CoF (0.2) and wear rate (10⁻⁴-10⁻⁵mm³/Nm) and ascribed to the formation of the glaze film consisting mainly of CaCrO₄ and CaMoO₄ on the worn surfaces. |
| Zhu et al. [84] Journal of tribology (2015) | Hot press sintering NiAl-Cr-Mo-CaF ₂ -Ag (10-20 wt.% of Ag) | Ball on disc from RT to 1000 °C, speed 0.2 m/s, load 10 N, testing time 30 min / Si ₃ N ₄ ball | <ul style="list-style-type: none"> Composite with 10 wt.% Ag provides self-lubricating properties from RT to 1000 °C and attributed to the synergistic effect of Ag, CaF₂, CaCrO₄ and CaMoO₄. |
| Liu et al. [85] Tribology International (2014) | Hot press sintering NiAl-(5-15wt.%) AgVO ₃ | Pin on disc from RT to 900 °C, speed 0.28 m/s, load 2 N, testing time 60 min / Inconel 718 disc | <ul style="list-style-type: none"> NiAl-Ag₃VO₄ composites have shown better tribological properties from RT to 900 °C due to the temperature adaptive action of the Ag, Ag₃VO₄ and AgVO₃. |
| Shi et al. [128] Wear (2014) | Spark plasma sintering NiAl-Ti ₃ SiC ₂ -MoS ₂ /WS ₂ | Ball on disc from 30 °C to 800 °C, speed 0.2 m/s, load 10 N, testing time 80 min / Si ₃ N ₄ ball | <ul style="list-style-type: none"> Composites with Ti₃SiC₂-MoS₂ exhibited excellent self-lubricating and anti-wear properties over a wide temperature range. MoS₂ lubricated better at low temperatures, while Ti₃SiC₂ lubricated better at high temperatures. |

The exhaustive research offers a helpful roadmap for developing a solid-lubricating composite that can withstand extreme temperatures. Solid lubricants have a significant impact on tribological behaviour, and the combination of silver and fluorides provides the best synergetic lubricating action, while reinforcements have a greater impact on tribological and mechanical properties, suggesting that metal alloying phases are more beneficial to ceramic phases.

The low coefficient of friction across a wide temperature range is mainly attributed to the integrated factors. These factors include:

- i. Tribo-chemistry:** At high-temperature environments, fluorides react with alloying elements to produce inorganic salts with high-temperature lubricous properties.
 - ii. Tribo-transfer:** At various temperatures, specific transfer films play a protective role, such as Ag-rich and fluoride-rich transfer film at low to moderate temperatures, and the lubricating film containing inorganic salts at high temperatures. These film acts as protective covers, reducing the direct between the mating pair.
 - iii. Tribo-glaze:** At elevated temperatures, a glaze layer forms on the worn surface. This layer is a complete and continuous oxide layer comprised of oxides and inorganic salts with lubricous properties. The glaze layer serves functions of both wear resistance and friction reduction.
 - iv. The synergistic action:** The lubricating properties across a broad temperature range are primarily the result of the synergistic action of Ag, fluorides and inorganic salts. These compounds develop various lubricous films depending on the testing temperature, influenced by friction forces, lubricant diffusion and tribo-chemical reactions.
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2.7 Formulation of the problem

In spite of the advances made in the direction of high-temperature self-lubrication, it has been a challenging task for tribologists and engineers to ensure effective lubrication of moving parts at higher temperatures. However, the quest is still on and researchers are trying to synthesize composite materials or coatings that are able to provide self-lubrication over a range of temperatures from room temperature to 800 °C. In this context, the development of composite materials containing a combination of solid lubricants is a promising approach that offers continuous lubricant replenishment at the sliding surface instead of relying on coatings due to their limited lifespan.

An extensive examination of existing literature indicates that limited research has been conducted to examine the friction and wear of Ni₃Al-based composites that incorporate a blend of Ag-WS₂, Ag-Cu-modified *h*BN (Cu-*h*BN) and WS₂-Cu-doped *h*BN (Cu-*h*BN) as solid lubricants across a broad temperature range spanning from room temperature (RT) to 800 °C. Silver (Ag) offers lubrication up to 500 °C by providing a lubricating film at the sliding interface at relatively lower temperatures and due to its high diffusivity at higher temperatures. The presence of Ag also facilitates the formation of a beneficial glazed layer of silver molybdates (Ag₂MoO₄ and Ag₂Mo₂O₇) at temperatures ranging from 600 °C to 800 °C due to a tribo-chemical reaction, which helps in reducing the coefficient of friction and wear rate. Tungsten disulphide (WS₂), owing to its layered structure, forms an easy-to-shear film at the contact interface of mating materials and maintains its lubricating properties at high temperatures due to its higher oxidation temperature of 539 °C, which is higher than graphite (325 °C) and MoS₂ (370 °C). Hexagonal boron nitride (*h*BN), possessing a lamellar structure, has also been reported to be a promising high-temperature and clean solid lubricant due its high thermal stability, good chemical inertness, and high thermal conductivity. However, its poor sintering and wettability characteristics have

restricted its use in the composite or coating. A few investigations have reported an improvement in the sintering and wettability features by modifying the surface of *h*BN with Cu or Ni. Since Cu and Ni are mutually soluble in each other, the modification of *h*BN with Cu is expected to improve the sintering characteristics and wettability as well as interfacial bonding between the modified *h*BN and Ni₃Al matrix. Hence, in the present study, an effort has been made to modify *h*BN by Cu to improve its sintering characteristics and wettability. The present study is aimed at fabricating the self-lubricating Ni₃Al-based composites containing lubricating species i.e., Ag, WS₂ and Cu-*h*BN and a combination of Ag-WS₂, Ag-Cu-*h*BN and WS₂-Cu-*h*BN via vacuum hot pressing and exploring their lubrication potential under dry sliding conditions at different temperatures i.e., RT, 200 °C, 400 °C, 600 °C, and 800 °C. The *h*BN powder has been doped with copper to overcome the poor integrating properties of *h*BN with the matrix. The combination of Cu and *h*BN results in the formation of a hybrid nanomaterial (Cu-doped *h*BN) which is expected to provide enhanced lubricating capability in comparison to the individual ones. This hybrid material can find potential applications in various sectors such as aerospace, automotive, manufacturing etc. It may also be used as a lubricant in engines and other machines to lessen the tribological problems and to improve their efficiency. This material may also be used in coatings or as a reinforcement in composite materials for high-performance applications. The WS₂ will provide excellent wear resistance, while the Cu-doped *h*BN is expected to provide thermal stability and low friction in the composites. Additionally, the investigation also intends to ascertain the prevailing wear and lubrication mechanisms due to the formation of compounds by tribo-chemical reactions and to examine the possibility of a synergistic relationship between Ag-WS₂, Ag-Cu-*h*BN and WS₂-Cu-*h*BN in attaining low friction and wear over an extended range temperature.

2.8 Objectives of the study

In view of the above, the present study has been carried out with the aim to fulfil the following objectives:

- (i) To synthesize the Ni₃Al intermetallic compound by ball milling and to characterize the same.
- (ii) To synthesize the Cu-modified or doped *h*BN nanosheets (Cu-*h*BN) through ultrasound-assisted exfoliation and chemical treatment with Cu-salt and to characterize its structural features.
- (iii) To fabricate Ni₃Al-based composites containing Ag, WS₂, Cu-*h*BN, Ag-WS₂, Ag-Cu-*h*BN and WS₂-Cu-*h*BN by vacuum hot press sintering and to analyze their microstructural features, density and hardness.
- (iv) To evaluate the tribological behaviour of Ni₃Al-based self-lubricating composites at RT, 200 °C, 400 °C, 600 °C and 800 °C by carrying out dry sliding wear tests at constant normal load, speed and sliding time and to establish the dominating wear mechanisms.
- (v) To examine the occurrence of synergistic action between a combination of solid lubricants like Ag-WS₂, Ag-Cu-*h*BN and WS₂-Cu-*h*BN in accomplishing effective lubrication from RT to 800 °C.