INFLUENCE OF LASER NITRIDING ON MECHANICAL AND WEAR BEHAVIOUR OF HIGH-SPEED STEEL

A THESIS

Submitted in fulfilment of the requirements for the award of the degree of Masters of Science (Research)

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CANDIDATE'S DECLARATION

I hereby certify that the work which is being presented in the thesis entitled "INFLUENCE OF LASER NITRIDING ON MECHANICAL AND WEAR BEHAVIOUR OF HIGH SPEED STEEL" in the fulfilment of the requirements for the award of the degree of Master Of Science (Research) and submitted in the Discipline Of Mechanical Engineering, Indian Institute of Technology Indore is an authentic record of my own work carried out during the time period from July 2020 to June 2022 under the supervision of Dr. Girish Verma, and Dr. Dan Sathiaraj, Department of Mechanical Engineering, Indian Institute of Technology , Indore. The matter presented in this thesis has not been submitted by me for the award of any other degree of this or any other institute.

(Yashaswi Malve)

This is to certify that the above statement made by the candidate is correct to the best of my/our knowledge.

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Abstract

Laser Nitriding is a well-known process to improve the hardness and wear resistance of steel. In this experimental work, laser nitriding was performed on high-speed steel by flowing nitrogen gas over the surface. Laser energy was used to irradiate high-speed steel surface by short laser pulses in nitrogen atmosphere. The experimental study was carried out at various processing parameters such as laser fluence (J/cm²), nitrogen flow rate (l/min) and scan speed (mm/s). The surface roughness, microhardness, and wear behaviour were measured and compared to evaluate the effect of nitriding parameters on responses. Furthermore, optimum nitriding parameters were obtained which resulted in enhancement of surface hardness by 42 % as compared to untreated samples. The wear loss was found to be decreased by 58% in the laser nitrided sample (0.0007mm³) as compared to the untreated sample (0.0017 mm^3) . The higher wear resistance and higher hardness were attributed to the nitride layer formed. The formation of nitride layer on the substrate material (high-speed steel tool) was confirmed using Field Emission Scanning Electron Microscopy (FESEM), Electron Dispersive Spectroscopy (EDS) and X-ray diffraction analysis. Hence, laser nitriding in open environment was found to be a promising method to improve the mechanical and tribological properties of high-speed steel.

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Chapter I: Introduction

High-speed steels can be defined as iron-base alloys composed of carbon, vanadium, tungsten, molybdenum and cobalt [1]. Because of the high amounts of chromium and nickel in the high-speed steel, it has good hardness and wear resistance, making it appropriate for a variety of engineering applications, such as machining [2]. Cutting ability is the most significant attribute of high-speed tool steel. Cutting ability is based on various mechanical properties like hardness, toughness, wear resistance, hardenability and the ability to withstand higher temperatures without losing its mechanical properties [3]. High-speed steels are currently divided into more than 40 categories based on their structure and characteristics. Many high-speed tool steels share numerous mechanical and physical characteristics. Properties may differ significantly depending on the varied chemical makeup. Moreover, the mechanical properties are highly influenced by the chemical composition of the steel [4]. According to the chemical composition and mechanical properties, high-speed steels are classified into different categories that are discussed below:

1.1 Classification of steels

1.1.1 High Carbon / D series: These steels are also known as secondary hardening steels. Some alloy carbides will occur during the tempering process. In other words, the hardness value of steels will rise to create huge volumes of alloy carbides, resulting in excellent wear characteristics. These steels contain 0.6 to 1.25 % of carbon and 97 to 98.6% of iron. These steels are also known as tool steels and are mainly used as cutting tools. Example: AISI U13, AISI S70C.

1.1.2 Chromium Hot-Work Die Steels: Forging, aluminum extrusion, shot sleeves, magnesium die-casting, and aluminum die-casting are some of the hot work applications for this category of steel. These steels can be hardened and will do so over time (as quenched to

approximately 55HRC depending on the maximum cross-sectional thickness). These steels contain 0.4 to 3.25 % of chromium and 96 to 97.8% of iron. Example: AISI H10, AISI H13.

1.1.3 Molybdenum High-Speed Steels: Molybdenum is a carbide-forming element that is primarily responsible for formation of blocky carbides like MC that are finely distributed throughout the steel matrix. With these steels, care must be taken while selecting the austenitizing temperature and holding time at that temperature. These steels are used in the manufacturing of cutting tools like saws and drills. These steels contain 3.5 to 10% of molybdenum and approximately 90 to 97% of iron. Example: AISI R6M5, AISI R6M5K5

1.1.4 Tungsten High-Speed Steels: Tungsten is a powerful carbide-forming agent that produces extremely high hardness values in steels. This group of steels can be used to cut at high temperatures without losing their hardness value. The tungsten series has less abrasion resistance than the Molybdenum series steels. These steels are used in manufacturing dies, punches, milling cutters and various delicate cutting tools. These steels contain 2 to 18% of tungsten and 92 to 97% of iron. Example: AISI M2, AISI K5

1.1.5 Low Carbon Steels: These steels are mainly used as mold materials in mass production processes. These steels necessarily need laser treatments or surface coatings to enhance their surface properties making them suitable as molds. These steels contain 0.04 to 0.3 % of carbon and 97 to 98.8 % of iron. AISI P21, AISI P20 are some common examples of these types of steels.

1.2 Microstructure of high-speed steel

The microstructure of high-speed tool steels contains of martensitic matrix with a distribution of two types of carbides known as primary and secondary carbides and retained austenite. The embedded carbides are also called blocky carbides and they consists of different crystal structures, morphologies and chemical compositions. The designation of these carbides is M_xC ,

where M represents one or more metallic atoms [5]. When using the X-ray diffraction method and treating M as a single metallic atom, these carbides can be quickly detected. The majority of these carbides, which are often found on the grain boundaries, are made of vanadium, molybdenum and tungsten. The carbides can be identified based on their color and shape. Mainly MC, M₆C and M₂C carbides are formed in the microstructure. According to the literature MC carbides consist of very less amount of iron. MC carbides have hardness of 2300 HV to 2500 HV. It is mainly composed of vanadium, molybdenum and tungsten. These carbides are black in colour and have fan like morphology as shown in Figure 1.1. The M₆C carbides have hardness in the range of 1400 to 1600 HV. They are white to light grey in colour as shown in Figure 1.1. These carbides have the morphology of the fish bone structure. Hardness, morphology, atomic element contrast are some characteristics on the basis of which carbide types are identified.



Figure 1.1 Microstructure of high-speed steel [1]

These carbides provide hardness, wear-resistance and excellent cutting ability to high-speed steels. Blocky carbides perform the function of protecting the matrix from wear and the secondary carbides provide high hot strength to the steel matrix. Changing the amount of

carbides can alter the mechanical properties of high-speed steels. The microstructure of the untreated high-speed steel is shown in Figure 1.1.

1.2.1 Composition of high-speed steel

The AISI developed a system of classification for high-speed tool steels a long time ago. This system comprises letter T for the steels which have tungsten as one of the main alloying elements and letter M for the steels which contains molybdenum and its alloys as one of the prime alloy elements [6]. Also, there is a certain number which follows either M series or the T series. Hence the high-speed tool steels are designated Ml, M2, Tl, TI5, and so on. This number does not represent any type of special significance other than to differentiate one type from another. For example, the type M1 does not reveal that it is alloyed with more elements than M2 or has higher hardenability values or less wear resistance or any other properties. It only helps in distinguishing the types and aims to simplify the selection process for the user [7]. The steels of the T series generally contain 12 to 20% of tungsten with substantial amounts of vanadium, chromium, and cobalt as the other alloying elements. Steels of the M series steels generally contains approximately 3.5 to 10% of molybdenum, with vanadium, chromium, tungsten, and cobalt as other alloying elements [8]. All the types of steels, whether it is molybdenum or tungsten, contain about 4 to 6% of chromium; 0.5 to 0.8 % of carbon and 0 to 1% of vanadium. It is observed that when the vanadium content is increased, then the carbon content is also increased [9].

A variety of elements are used as alloying agents in the manufacturing of M and T series highspeed tool steels to provide the desired properties to these tool steels.

1.3 Surface Treatment Processes

In industrialized cultures, surface treatments and coatings are utilized more and more frequently to decrease or regulate friction and engineering material wear. The other driving force of this process is tied to economic and environmental factors [10]. Examples include the requirement to lower the cost of repairing worn machine parts, to optimize energy utilization and increase productivity and to avoid the use of lubricants as they are harmful for the environment. Wear plays an important role when it comes to reduce the cost of worn-out specimens. Proper improvement of the wear and tribological properties of the tool can lead to increased productivity. For making a tool which is wear resistant, it should have excellent mechanical strength, high hardness value, high toughness value and should be chemically stable [11]. In the conventional as well as non-conventional manufacturing processes, it is quite difficult to obtain all the properties in single tool material. Hence, surface engineering is proven to be an important technique so as to obtain a tailor designed material with desired properties [12].

The functional properties of such materials could be easily optimized in surface engineering technology [13]. For example, during the designing of cutting tools, the tool material should be selected to provide strength and toughness during cutting while the coating could be customized to reduce friction and provide high wear resistance during the cutting operation [14]. Hence surface engineering could be the key for improving many properties like wear resistance, hardness and corrosion resistance. The improvement in surface properties can be achieved with different processes like:

1.3.1 Surface Coatings: The deposition of a layer of material on another material with the ambition of producing the desired surface properties is known as the concept of coating. Coatings can be of various types depending on the variety of materials used in it. A single layer coating consists of one material deposited over another material while multi-layer coating

consists of two or more materials deposited over the material in one or two layers. TiN, TiAl, TiC etc. are the materials which are used in single or multi-layer coatings.

1.3.2 Laser Shock Peening: The laser shock peening process induces compressive residual stresses into the material due to which the crack propagation gets impeded and the life of metallic components is increased. A high energy pulsed laser is used in the process to create a high amplitude stress wave or shock wave. When these shock waves impact the surface, it propagates through the material. It causes the surface layer yielding and produce a compressive residual stress.

1.3.3 Cryogenic Cooling: By far, cryogenic cooling is thought to be the most adaptable way to machine different kinds of technical metals and alloys. During the cutting procedure, liquid nitrogen is applied directly to the cutting zone. This procedure can lessen the cutting forces impact as well as the coefficient of friction between two sliding surfaces. It has been shown to greatly reduce the likelihood for welding between the tool and the work piece material. Apart from this it also increases the hardness of the cutting tool and the work piece material.

1.3.4 Surface Texturing: Surface texturing is the process of surface alteration by forming textures on the surface with the help of non-conventional machining processes. The process consists of surface remelting, which in turn decreases the surface hardness and produces residual stresses which are tensile in nature. The textures can be of different types like micro dimples, micro grooves, microchannels These textures have different impact on wear and tribological properties. Surface texturing helps in tool life enhancement by reducing tool wear. It also enhances the tribological properties of the tool material.

1.3.5 Nitriding: Nitriding is well known surface treatment which is thermochemical in nature. It involves diffusion of nitrogen in the top surface to metals to obtain surface hardening and enhanced tribological properties. Nitriding uses laser, gas or plasma for irradiation of the

material and hence it could be of various types. Some of the nitriding techniques that are primarily utilized are salt bath nitriding, plasma nitriding, gas nitriding, and the innovative process laser nitriding.

1.4 Introduction of nitriding

Nitriding is a well-known thermochemical surface treatment developed in the early 19th century which is used prominently in several industrial applications such as aerospace, automotive, turbines, bearing and cutting tool manufacturing applications [15]. From the metallurgical point of view, nitriding is a thermochemical process, where nascent nitrogen gets diffused into the metal subsurface to form hard thin nitride layer over the surface [16]. Depending on the heat source and methods, the process of nitriding is classified in various types.

1.4.1 Salt Bath Nitriding: The salt bath/liquid nitriding consist of three steps which are degreasing, preheating, and nitriding. Degreasing is performed to get rid of the unwanted contamination from the surface. Preheating is performed to avoid moisture from the surface. Then nitriding process is performed in molten salt at a temperature range of 550 - 650 °C for 3 to 5 hours. During this process, the parts are immersed in nitrogen-containing salts like Na/K-cyanide which also contains reducing agents like Na/K-CO₂. These salts get decomposed at elevated temperatures and the nitrogen atoms gets diffused on an atomic scale to form a thin nitride layer on the substrate material. Although salt bath nitriding obtained significant importance in the past few years, still there are few limitations which needs to be considered for its application. Any source containing enough amount of nitrogen and carbon will release harmful cyanide gas when it is subjected to any heat-treatment process. The salts used for the liquid nitriding process are toxic in nature and can act as poisoning substance which prevents the human body tissues from absorbing oxygen [17].

1.4.2 Plasma Nitriding: Plasma nitriding or ion nitriding is also called as glow discharge nitriding process. This process is usually conducted in a vacuum chamber. Setup of this process comprises a pumping system which controls the chamber pressure and a plasma generator. Two furnaces are used in the plasma nitriding process which are cold-wall furnace and hot-wall furnace. The ignition of plasma takes place between the furnace wall and the metal mesh, which acts as a cathode. The plasma nitriding uses pure nitrogen gas as a source of nitriding rather than ammonia (NH₃) which is used in the gas nitriding process. It should be noted that the reactivity of nitrogen gas is not due to the temperature rather due to the ionized gas molecule known as plasma. The bias in applied voltage between furnace and metal makes the ions accelerate towards the substrate surface. The thickness of compound layer can be altered by changing the value of the applied bias voltage and plasma power density [18].

1.4.3 Laser Nitriding: The principle of laser nitriding involves four steps known as laserinduced heating and melting of the metal surface, generation of nitrogen plasma over the surface, chemical reaction between plasma and the melted liquid metal, and finally quick solidification followed by the formation of a hard nitride layer [19]. In the nitrogen atmosphere, the top surface of a high-speed steel sample is scanned by a focused laser beam. As the laser beam is focused on a particular desired spot on the sample surface, high temperature is generated. When the temperature of the laser beam on the surface reaches melting point of material, it melts and evaporates the material from the top surface and plasma is formed [20]. The melted material reacts with the ionized nitrogen atoms in the presence of plasma and the rapid formation of a thin nitride layer takes place.

As the focused beam of laser irradiates the metal surface, optical properties of the metal such as reflectivity, absorptivity, and transmissivity of material plays key role in the process. In metals, the mechanism of energy absorption can be described by the activity of free electrons [21]. Initially, the photon energy indented from the laser gets absorbed by the free electrons in the metal and localized heating increases due to electron-electron and electronphoton interactions according to the inverse bremsstrahlung principle. The required time for the excited electrons to transfer their energy to photons is material-specific. For most of the metals, the thermalization time is of the order of 10 to 12 seconds. However, the absorption of photon particles causes the incident laser beam intensity to decrease with the penetration depth in the material. The penetration depth of the material is generally quantified in the terms of absorption coefficient (α). The absorption coefficient is purely dependent on the temperature, wavelength, and surface chemistry of the material. However, for constant α value, decay in the intensity is an exponential function of the penetration depth (z) and can be defined by Beer-Lambert's law. It follows:

$$I(z) = I_0 e^{-az}$$
 [Equation - I]

Io - represents the intensity just inside the surface after the reflection loss. Nitriding has been reported to enhance the wear and mechanical properties of all types of high-speed steels

1.5 Wear Mechanism

All the surface treatment processes are performed to enhance the wear resistance. Wear is of great economic importance since the cost of wear is very high. Hence, enhancing the wear resistance is a main reason behind performing surface treatment process. To understand wear, it is important to understand the conditions under which material wears and also the mechanism behind it.

Wear is defined as removal of material from the contact surface as a result of sliding, erosion, abrasion, adhesion or friction [22]. Apart from corrosion and breakage, wear is also considered as a main cause of failure of many tools and engineering materials like cutting tools, brake shoes and pads. The statistical analysis on wear of engineering materials also reveals that wear

is responsible for the failure of machines more than corrosion. The cost of wear not only include the cost of worn-out specimen but also the cost of replacement of new specimen. The cost of wear also includes the cost of lost production, the machine downtime cost, cost of products produced with poor preciseness because of the worn-out tool [23]. Hence, controlling wear of tools and components can result in significant savings. One main reason behind the coatings and various types of surface treatments is mainly to reduce the amount of friction as well as to reduce wear. Wear happens in three stages as a function of time and sliding distance [24]. The first stage of wear is known as running-in stage which involves primarily adhesion, abrasion or combination of adhesion and abrasion wear mechanism. The second stage of wear is knownas steady stage. This type of wear occurs throughout the complete lifecycle of the component. The type of wear happening in this cycle is low but gradual and continuous throughout the lifecycle. The wear rate of the component gets rise again and third body mechanism comes in to the play. The third stage of wear is catastrophic in nature. According to the wear theory, thereare certain mechanisms designed according to which wear occurs in any material.

1.5.1 Adhesive Wear

This type of wear involves interlocking of the interfacial surfaces which come in contact with each other. As the normal load is applied on the surface, the local pressure also increases at the asperities [25]. Because of this pressure, it leads to an increase in the yield stress followed by plastic deformation of the asperities [26]. As a result, the area of contact increases. In the absence of any kind of lubrication, the asperities come into direct contact and because of the load, they form a cold-welded joint. The joint starts to shear and it develops new junction. Sliding surfaces are destroyed by this wear mechanism. This mechanism also produces wear particles which in turn causes severe cavitation inside the surface. Sometimes, the cavitation is so large that it causes the failure of the functioning components. Archard equation describes the wear rate in this type of wear as W = k (N/H). Here, W represents the wear rate, k is the

coefficient of wear, N is the normal load applied and H represents the hardness value of the softer material.

1.5.2 Sliding Wear

When the two surfaces in relative motion under load leads to the friction induced damage on either surface then it is known as sliding wear. Accordingly, it is seen that the wear and induced friction of any sliding couple are contributed by several properties, such as surface finish, load, speed, shape and dimensions of the coupled solids, adsorption of atoms, type and nature of surface films, temperature, humidly, lubrication, material composition and metallurgical parameters [27]. Sliding wear can be performed at the laboratory scale by using several test configurations viz. pin-on-disc, ball-on-disc, block-on-ring, etc. Based on the type of material removal, the nature and properties of the mating solids, loading conditions and reaction products different material removal mechanisms are be classified as adhesion, abrasion, surface fatigue, tribo-chemical wear, delamination theory and galling effect [28]. Abrasive wear is the part of sliding wear. Abrasive wear is the kind of wear that happens when a surface loses material as a result of coming into contact with another surface made of a tougher material. Because of this contact the softer material gets abrased and it leaves some particles of itself which is known as debris between two surfaces. This type of wear is also called gouging, scratching or scoring on the basis of the volume of eroded material. Two categories of abrasive wear exist: two-body abrasion and three-body abrasion. Two-body abrasion refers to the kind of wear that happens when one of the contact surfaces is substantially harder than the other surface. Grinding, milling, and cutting are a few instances of two body abrasion. In three body abrasion, the third body which is a small grit of particle or part of any abrasive separated from the surface, gets lodge between any two soft sliding surfaces and when it comes in motion it abrades one or sometimes both of the surfaces [29].

1.5.3 Surface Fatigue

Surface fatigue is the formation and travelling of cracks in surface region which are developed due to repeated tribological stress cycles (e.g., reciprocator motion at a loaded tribo-contact) [30]. Localized asperities may provide sufficient stress cycles on the contact surfaces at microscopic scale [31]. The fatigue of materials proceeds in the sequence of elastic deformation followed by plastic deformation, strain hardening and strain softening, formation of cracks and then and propagation of cracks. This process is significant at low loading and low tendency of adhesion between surfaces having hardness difference [32].

1.5.4 Fretting Wear

Fretting wear occurs when two surfaces have oscillatory relative motion in respect of each other with small amplitude. Depending upon the amplitude of the relative motion, the wear canalso be applicable to the conditions of adhesive wear.

1.6 Delamination theory of wear

The delamination theory of wear claims that the softer surface layer continuously deforms as a result of the instability of many dislocations, which causes low-speed sliding wear of the material. It begins as the nucleation of a subsurface fracture and then spreads outward along the surface [33]. The delamination theory of wear bases its argument on:

(a) Dislocations are produced in the material's sliding surface during the sliding wear state as a result of the surface's plastic deformation. The slider also breaks through the oxide layer, exposing a brand-new material surface layer. The image force then removes the dislocations that are almost parallel to the surface. Following that, there is less dislocation density close to the material's surface [34].

(b) During the continuous sliding wear there are piles up of dislocation at a particular distance. This causes voids to build over time, and the formation will be accelerated if the material has a hard second phase for dislocations.

(c) Void formation is possible as a result of the plastic flow of matrix close to the particles.

(d) As time goes on, the spaces get larger or the metal surface shears, causing them to consolidate. This causes a crack to appear along the worn surface.

(e) The material between the fracture and the surface will start shearing when this crack reaches a specific length (which depends on the substance), creating a sheet-like particle. This delamination hypothesis of wear is only applicable to low-speed sliding wear, where the rise in temperature at the contacting surface is so minimal that diffusion, phase change, and diffusion do not occur during the wear process [35].

The wear of tools in industries decreases the productivity, increases the cost of production as well as it is highly detrimental from the environmental point of view. Tools which are worn out no longer perform the function and it is not always easy to dispose them. The worn-out tools which are functioning, not only create faulty products but also produces chatter sound and decrease the damping quality of the machine. If such tools are used in the production process, they cause the failure of machine and decrease the quality of the manufactured products. Wear is highly undesirable in any production process. The main aim of all the surface treatment processes is to impart the wear resistance properties to the material. Nitriding, cryogenic cooling, cryogenic treatments and all various techniques tries to increase the wear resistance. Through nitriding it has been observed that the wear resistance is increased.

Chapter II: Literature Review

Nitriding is known to be an effective surface treatment to enhance the mechanical and tribological properties of irons and steels since ages. Nitriding alters the properties and microstructure of steels with the introduction of nitrogen and increases the amount of carbides with various types of precipitations. In past, the surface morphology of various nitrided steels has been studied by many researchers. Most of these studies have evaluated the effect of laser nitriding on steel and found enhancement in different mechanical properties. This section presents a comprehensive review of all the studies reported on nitriding of different types of steels and iron.



Figure 2.1 Microstructure of active screen plasma nitrided high speed steel [18] Doyle et al. performed active screen plasma nitriding on high-speed steel at a high nitriding temperature of 570°C. They have found that an acicular structure was formed up to a depth of ~ 30 μ m indicating the presence of nitrogen. The scanning electron microscopy microstructure obtained in this research work is shown in Figure 2.1. This microstructure revealed an increased amount and non-homogenous distribution of carbides inside the martensitic matrix post laser nitriding process. The corrosion, mechanical, and wear resistance of the alloy were significantly improved by the plasma nitriding method on high-speed steel. The formation of the FeN compound layer was responsible for the improvement in wear resistance. Still the preciseness of the process was not very high. Undesired heating was also observed during the process [18].

Shin et al. reveals the microstructure of the laser nitrided AISI P21 mold steel. The packets of needle shapes precipitates were observed. The thickness of layer of laser nitriding was 100-300 nm to the depth of ~15 μ m was measured [36]. The cross-sectional microstructure obtained after the laser nitriding process is given in Figure 2.2.



Figure 2.2 Cross sectional microstructure of laser nitrided AISI P21 mold steel [36] In this experiment the change in wear resistance of laser nitrided AISI P21 steel was also studied. In the pin-on-disk test the laser-nitrided P21 steel showed 18.9% less wear than the base metal. The production of AlN precipitates was attributed to the increased hardness of laser-nitrided P21, which improved the wear resistance [36].

Yan et al. compared the tribological behavior of AISI P20 steel to the gas nitrided AISI P 20 steel. The tests were carried out at normal load of 200 N for 60 minutes with a sliding distance of 1400 m. The wear resistance was significantly improved by the gas nitriding treatment due to the increased nitrogen content in surface material [37].

Godec et al. studied the wear properties of plasma nitrided 316L stainless steel. The sliding wear test was performed on 20 N load for 833 seconds with a sliding distance of 100 m. The wear volume was found to be decreased significantly post plasma nitriding due to the formation of the nitride layer [21].

Psyllaki et al. performed parametric study on laser nitrided AISI 3115 steel. The parameters under study were laser beam power, number of successive passes, way of nitrogen supply and laser beam scanning velocity. The optimum laser beam power was found to be around 1 kW. At lower powers no modifications were found and at higher power the surface melted undesirably. It was also found that nitrogen should be supplied vertically to achieve higher thickness of nitride layer [38].

Kulka et al. analyzed the effects of laser beam power on AISI 4140 steel on a CO_2 laser. It was revealed that laser power in the range of 115 W to 238 W is able to produce the desired thickness of nitride layers [39].

Schaaf et al. performed laser nitriding of high-speed steel with single spot irradiation method using excimer lasers. The analysis of the fall out material revealed the formation of FeN phase. This process necessitated the use of vacuum nitriding chambers which complicates the process as well as is a big challenge for the commercialization of the process [15].

Laser Nitriding of steel was performed by Schaaf et al. in long nitriding cycles which lasts 36 hours to 40 hours with the heating period of 24 hours. This experimental work revealed the formation of FeN, increased hardness and wear resistance yet the process involves very long nitriding cycles which is not practically applicable in the future [16].

Sim et al. studied the microstructural and mechanical properties of laser nitrided AISI P21 steel. In this study, to ensure homogenous nitrogen flow, authors used high power diode laser system with vacuum chamber. Up to 40% increase in hardness was obtained through the process as the same was attributed to the formation of AIN precipitates. The setup of experiment ensured homogeneous nitrogen flow, still the use of vacuum chamber is a part of very conventional setup which is a constraint in the applicability of the process [40]. Yilbas et al. performed laser nitriding on AISI H13 tool steel (a type of high carbon high speed steel). Nitrogen assisting gas was targeted on the sample surface coaxially with CO₂ laser. They found that the residual stresses induced due to laser nitriding were tensile in nature. The fracture toughness of the material was reduced due to the formation of brittle structure on the surface. Young's modulus increased up to the value 230 GPa from the base value (190 GPa). Figure 2.3 represents the surface morphology obtained after laser nitriding process. The surface is appearing feathery due to the presence of nitride rich grains (ϵ -FeN and ϵ -Fe₃N) and the diffused nitrogen at the grain boundaries in the white / compound layer. In X-Ray diffraction analysis, γ - Fe₄N peaks were obtained which indicated the presence of nitride precipitates in the diffusion zone [41].



Feathery Like StructureFine Elongated Grains StructureFigure 2.3 Microstructure of laser nitrided AISI H13 tool steel [41]

Shin et al. analyzed the effect of laser nitriding on NAK80 steel. The setup of nitriding involves a closed vacuum chamber filled with nitrogen. They found the formation of AIN precipitates on the surface and it was attributed with the increase in microhardness. Elemental segregation was also confirmed in the precipitates formed in laser nitriding. This experimental work, besides belonging to very recent times, involves the use of vacuum chamber method, which decreases the ease of application of laser nitriding process [42].

Jendrzejewski et al. performed laser nitriding on 38HMJ steel. The samples were kept in a liquid nitrogen bath and irradiated with a CO₂ laser beam. In order to avoid contamination, it was shielded by Argon flow. The results were compared with that of standard gas shielding process. The results showed that in laser nitriding process, the volume of heat affected zone was reduced in comparison to the standard gas shielding process as well as higher hardness was obtained. Electron spectroscopy confirmed the local nitrogen enrichment of the laser treated areas but the distribution of the nitrogen content over the scanned surface was found to be non-uniform. It was due to the changes in diffusion coefficient which depends on the local processing temperature. Hence, this experimental setup does not allow the user to have precise control over the local processing temperature throughout the process. Further experimentation is required to obtain homogenous nitrogen distribution over the entire surface [43].

Boztepe et al. performed a comparative investigation of the corrosion and mechanical behaviour of nitrocarburized, gas nitrided, fluidized-bed-nitrided and plasma nitrided mold steel (Impax supreme which is equivalent to AISI P20). The surface treatment processes were performed in industrial gas nitriding facility, fluidized nitrogen bed, vacuum and nitrocarburizing furnace in a long cycle of 8 hours. From the hardness profiles of samples obtained through all the process, it was found that the plasma nitrided samples have the highest hardness value and it was uniform all over the surface. It was found that plasma nitrided samples showed better corrosion behavior in terms of tendency to corrosion. In the plasma nitrided samples, the top layer was found to be a compound layer containing ε -Fe₂₋₃N, γ -Fe₄N and other nitrides. The compound layer determines the tribological and corrosion behavior. Beneath the compound layer, diffusion layer or diffusion zone was found which consisted of coherent nitride precipitates. The diffusion layer determines the strength and hardness of the material. Hence, Plasma nitriding was found to be more efficient than all other processes [44].

Jan et al. analysed wear and corrosion resistance of plasma nitrided and gas nitrided PM tool steel. The surface obtained through the two processes were very different from each other. Figure 2.4 shows the microstructure of layers prepared by both processes. The plasma nitrided layer consisted of two sublayers i.e., compound layer and diffusion layer. The compound layer consisted of carbonitrides and a network of γ -M₄N nitrides. Figure 1.2 shows microstructure of the compound layer. It was free from pores, homogenous and it protected the surface from corrosion. Beneath the compound layer, there was diffusion zone, consisting of a nitrogen solid solution in martensite and fine particles. In the gas nitrided samples, no compound layer was formed. The hardness value of plasma nitrided samples was found to be greater than that of gas nitrided samples. The higher hardness of the plasma nitrided samples is attributed to the diffusion zone. The difference in the outcomes of the processes is attributed to their different mechanisms. In plasma nitriding, the accelerated ions in glow discharge intensifies the whole process, while in gas nitriding only thermal movement governs the flux of nitrogen atoms. Hence, plasma nitriding turns out to be more effective than gas nitriding [45].





Microstructure of the layers formed by Plasma nitriding and gas nitriding

Microstructure of the compound layer formed by Plasma nitriding

Figure 2.4 Microstructure of plasma and gas nitrided PM tool steel [45]
Wen et al. evaluated the effect of nitriding temperature on the wear, corrosion and mechanical properties of plasma nitrided mold steel (NAK 55). Plasma nitriding was performed for 10 hours in a vacuum chamber with varying temperatures and it was found that with higher processing temperature, higher hardness and higher wear and corrosion resistance can be obtained. The nitrided layer consisted of a compound layer rich in ε -nitride and an adjacent diffusion zone. Increase in corrosion resistance is directly related to the increase in volume fraction of nitrides in the compound layer. Wear properties improved drastically when the surface layer consist of compact monolayer of closely packed hexagonal ϵ -Fe₂₋₃N phase. ϵ nitride protects the layer better than any other nitride. As the temperature increased, the thickness of compound layer increased. After the temperature was increased beyond 525°, denitriding and decarburization took place. The microhardness was increased up to 80%. It was concluded that processing at higher temperatures provides higher microhardness as on increasing the temperature, α -Fe decreases and ϵ -nitride increases. Also, the precipitates of iron, nitride and other metals are formed on the grain boundaries. These precipitates distort the lattice and pin crystal dislocations thereby raise the hardness and wear resistance of the surface. Hence, it was found that the process provides precise control over the surface properties through temperature control up to a certain limit [46].

Mudali et al. discussed various techniques of introducing high levels of nitrogen into steel surface. Ion implantation, laser alloying, laser nitriding can be effectively used to produce modified surfaces with novel microstructures to further improve the properties. In this review paper, surface alloying with nitrogen, plasma immersion ion implantation, plasma nitriding, diffusion annealing, gaseous nitriding, gaseous solution nitriding had been discussed with its applications, advantages and disadvantages. It is concluded that for selective alloying the surface with nitrogen, when the bulk properties need not be changed, lasers are an ideal tool.

Lasers are chemically clean, remote and non-contact process with feasibility of automation. In laser processing heat affected zone and thermal profiles can be controlled easily [47].

Obeidi et al. performed laser surface processing on 316L stainless steel with controlled nitrogen-argon concentration levels. Nitrogen is generally diluted with argon as it decreases the surface tension of the molten material, alloying the gas to penetrate deeper, however lower concentration of nitrogen can also result in lower hardness level. In this work a mixture of argon and nitrogen was delivered coaxially with CO₂ laser on the sample. It was found that after laser processing a martensite phase was formed with high value of hardness. However, no discernible nitrogen peak was observed in EDX analysis. Thus, it was concluded that nitrogen content is below the limit of detection. The hardness of material decreased with depth, but was significantly raised up to 400 micrometers. Hence, it can be concluded that laser processing creates harder martensitic structure, with the nitrogen a harder martensitic structure withgreater enhancement in mechanical properties could be produced [48].

In a recent review paper on laser nitriding and carburization, Hoche et al. discussed about the importance of nitriding, carburizing and different types of hybrid processes which are very effective surface treatments. However, the complicated setups involved in these processes makes them difficult and expensive to use in the industrial culture. The innovation in this area lies in the idea of a compatible and quick setup which can reduce the processing time and provides ease of access to the industries towards these novel techniques of surface engineering [49].

In this experiment the author tried to choose the experimental setup which reduces the effort in laser nitriding. Ease of application, precision, chemical stability, compatibility, replicability, and environment friendliness is the basis of choosing the modified setup of laser nitriding process.

Chapter III: Research Gap

Nitriding is a promising method to enhance the surface properties of iron and steels. Experimental findings have proved that nitriding of HSS improves wear resistance and other mechanical properties. From the literature it can also be seen that most of the reports are in the area of salt bath nitriding and plasma nitriding. On the other hand, the effect of laser nitriding has been explored thoroughly. According to available literature, one work has evaluated the effect of laser nitriding with single spot irradiation in closed nitriding chamber. However, no one has reported the effect of laser nitriding on HSS in open environment condition. In this research, the author tried to perform laser nitriding with a novel technique. This technique of laser nitriding eliminates the use of large vacuum chambers, complex setup as well as long nitriding cycles. Hence, the laser assisted nitriding technique used in this research work itself is a new concept. In this research work the wear analysis of the laser nitrided high-speed steel is also included which has been not reported by any of the authors before.

3.1 Basis of Choosing Laser assisted nitriding process

For nitriding, many techniques have been devised, including salt bath nitriding, gas nitriding, and plasma nitriding. The salt bath nitriding process generates dangerous chemical reactants like cyanide, which can have a negative impact on the environment and human health.

All these challenges can be easily eliminated by the application the novel method of laser nitriding. The laser nitriding procedure involves directing a laser beam at the top of the substrate while it is exposed to the air and nitrogen. Irradiation results in localized melting of the irradiated area, which speeds up the development of a compound nitride layer on top of the sample. During the laser treatment, the exact temperature control over the nitriding surface encourages the production of uniform compound layer thickness, which is very challenging to achieve during the plasma nitriding process. When compared to traditional nitriding techniques, laser nitriding is highly competitive, prevents unwanted heating, and is extremely precise [15].

The method used in this experimental work is completely novel since it is an open environment laser nitriding process which does not need any vacuums chambers or lengthy nitriding cycles. This method is practical and the setup of the process is easily achievable and applicable for large components. This can be a good solution for industries working on surface treatment of big components like big gears and bearings. Hence for the nitriding of high-speed steels the method of laser nitriding was chosen.

Chapter IV: Methodology

The experimental procedure of laser nitriding in an open atmosphere starts with preparing a high-speed steel sample. The sample is cut preciously into the desired shape and size. The sample's height is chosen so that the scanning electron microscopy and X-ray diffraction could be performed on it without any complication in the machine. After cutting of sample, it is prepared according to the standard metallographic technique. After the laser nitriding of a sample, it is characterized through FESEM and EDX analysis followed by XRD and roughness measurement. Afterward, mechanical testing of the sample is performed. At last, the tribological properties of the sample are characterized through a wear test. For each set of parameters, two samples are prepared and every test is repeated ten times on each sample. Hence the repeatability and replicability are checked throughout the experiment. The process chart given in Figure 4.1 gives a brief sequence of the laser nitriding process.



Figure 4.1 Process chart for laser nitriding

4.1 Sample Preparation:

The received samples from Miranda Tools private limited were cut into 10 mm * 10 mm * 4 mm using wire electrical discharge machining and prepared according to the standard metallographic techniques. The composition of the high-speed steel is given in Table 4.1. The mirror-polishing was obtained with 400-800-2000 grit polishing papers followed by polishing with the 1 μ m alumina suspension liquid. The mirror-polished samples were ultrasonically cleaned in acetone for 15 minutes to remove any undesired particles. After the sample preparation, the centerline average roughness value of the top surface of the sample was measured on a non-contact type surface profilometer (Veeco NT 9080). The centerline average roughness value obtained was ~ 10 μ m.

Table 4.1. Chemical composition of the high-speed steel Tool (wt.%)

Element	С	V	Cr	0	Co	W	Mo	Fe
Composition (wt.%)	0.6	3.4	4.1	7.2	7.2	9.2	3.2	Balance

4.2 Microstructural characterization

After polishing the samples, the Vilella's reagent was used as an etchant for 15 seconds to reveal the microstructure. The surface microstructure of the HSS steel sample was examined using field emission scanning electron microscopy FESEM (JSM - 7610FPlus). Figure 4.2 depicts a typical microstructure of the material obtained through FESEM.



Figure 4.2 Microstructure of the HSS tool at 500X

The microstructure of high-speed steel reveals the martensitic matrix with the distribution of different types of carbides in it. The distribution of the carbides inside the matrix was found to be non-homogenous. The primary blocky carbides of various types were identified in the microstructure, mainly white to light grey in color. MC, M₆C and M₂C were present in the microstructure. These carbides are composed of vanadium, molybdenum and tungsten. The carbides are responsible for the high hardness, good wear resistance and excellent cutting ability of high-speed steel. Changing the amount of carbides can alter high-speed steel's mechanical and surface properties.

4.3 Experimental Details:

Laser nitriding was performed in the open environment using a spectra physics pulsed Nd: YAG laser in Q switch mode. The nitrogen gas was supplied through a cryocan combined with a voltmeter. The gas flow nozzle had an inner diameter of 6 mm, and a distance of 10 mm was maintained between the tip of the nozzle and the sample surface. An angle of 45° was maintained between the tip of the nozzle and the surface of the sample. The nitrogen flow rate could be easily controlled by changing the voltage value. The sample was placed on the computer-controlled x-y moving stage. The laser beam diameter was set to 10 mm. The focal length of the convex lens was arranged to 20 cm so that the focused laser fell straight on the sample surface. The spot diameter of 0.3 mm was used, along with the depth of focus of 20 mm. The scan speed of the laser beam was constant at 1 mm/s while three varying fluences (J/cm²), 113.33, 84.88, 84.88, were chosen for the experiment. With these varying fluences, the nitrogen flow rate was kept variable at 15, 15, and 25 l/min values, respectively. The other process parameters used in the laser nitriding process are given in Table 4.2. The schematic diagram of the experimental setup is shown in Figure 4.3 and the experimental setup is shown in Figure 4.4.



Figure 4.3 Schematic diagram of experimental setup of laser nitriding process



Figure 4.4 Experimental setup of laser nitriding process

Laser Nitriding Process Parameters	Value
Pulse width (s)	9
Stand-off distance (cm)	30
Frequency (Hz)	10
Spot diameter (mm)	0.3
Wavelength (nm)	532
Laser fluence (J/cm ²)	113.18, 84.88 and 84.88
Scan speed (mm/s)	1
N ₂ gas flow rate (l/min)	15, 15, 25
Overlap Percentage (%)	30

 Table 4.2 Process parameters of laser nitriding

The parameters have been selected from the relevant literature[15]; however, the parameters have been modified according to the properties of high-speed steel. Some of the parameters have been evaluated by carrying out preliminary experimental work. The microstructural characterization of the samples was performed through field emission scanning electron microscopy coupled with energy dispersive spectroscopy. The setup of field emission scanning electron microscopy and energy dispersive spectroscopy is given in Figure 1.1 in the appendix section.

Grazing Incidence X-Ray Diffraction (GI-XRD) using Cu-K radiation at a 3° incidence angle was used to examine the formation of the new phases in samples. The X-Ray Diffraction setup is given in Figure 1.2 in the appendix section.

The centreline average roughness value of the samples was measured through a non-contact type profilometer. The setup of surface roughness measurement is given in Figure 1.3 in the appendix section. The centreline average roughness value of the laser nitrided sample was found to be ~ $0.9 \mu m$.

A microhardness test was carried out on a load of 2N on a Vickers pyramid indent tester. The setup of microhardness measurement is given in Figure 1.4 in the appendix section. The average hardness value was measured at ~873 HV as an average of 10 successive measurements.

High-speed steel's friction and wear characteristics were studied against commercially available WC balls of 10 mm diameter using a ball-on-disk tribometer (TR-201E-M2, DUCOM, Bangalore, India). A Linear reciprocating wear test was conducted on a ball on a disk tribometer with a load of 10 N for 15 minutes at 500 rpm. The setup of a ball on a disk tribometer is given in Figure 1.5 in the appendix section. The WC balls are 14 GPa in hardness. The high-speed steel samples and balls were cleaned with acetone in an ultrasonic bath for 15

minutes prior to tribological testing and then dried in a hot air stream. While the samples revolved at 500 rpm (a linear speed of 0.08 mm/s) to create a track radius of 3 mm, the WC ball was held stationary while the imposed load was applied. Throughout the test, a load of 10 N was used. The continually recorded frictional force was used to calculate the coefficient of friction (COF). The depth and width of wear scars were measured using a surface profilometer (Veeco NT 9080). Ten measurements per track were taken to determine the average width or depth, and wear volume (V) was calculated using the formula below:

where: Length of the wear scar (mm), breadth of the wear scar(mm), and d is the depth of the wear scar (mm).

Chapter V: Results and Discussion

5.1 Microstructural Characterization

The microstructure of the laser nitrided high-speed steel tool is given in Figure 5.1. The Figure depicts the microstructures obtained after laser nitriding at different laser fluences and variable nitrogen flow. Table 5.1 shows the value of laser fluence and nitrogen flow used to prepare the laser nitrided samples. The microstructure obtained after the laser nitriding process reveals an increased amount of carbide in comparison to the microstructure of the untreated steel. The surface morphology also appeared to be slightly rough. The fallout of the material on the surface was observed with uniform carbide distribution. The optimum thickness of the nitride layer formed was found to be ~ 40 μ m. The Energy dispersive spectroscopy micrographs observed that a maximum of ~ 32% nitrogen had been diffused in the top surface of the laser nitrided samples. The Energy dispersive spectroscopy micrographs are given in Figure 5.2. The results are in accordance with the past literature, where a maximum of 30% nitrogen was found after nitriding, and an increase in the amount of carbide was reported. Laser nitriding alters the microstructure of high-speed steel as it increases the amount of carbides and various precipitates of iron and nitrides are formed on the surface. The carbides identified after the nitriding process was mainly blocky carbides.

S.N.	Type of sample	Laser Fluence value	Nitrogen flow rate
1	Untreated Sample	-	-
2	Sample 2	113.18 J/cm ²	15 l/min
3	Sample 3	84.88 J/cm ²	15 l/min
4	Sample 4	84.88 J/cm ²	25 l/min

 Table 5.1 Parameters of laser nitrided sample



Figure 5.1 Microstructure of the HSS samples taken on magnification 500 and scale 10 μm
(a) Untreated (b) Laser fluence = 113.33 J/cm², Nitrogen flow rate = 15 l/min (c) Laser fluence = 84.88 J/cm², Nitrogen flow rate = 15 l/min (d) Laser fluence = 84.88 J/cm², Nitrogen flow rate = 25 l/min



Figure 5.2 Electron dispersive spectroscopy graphs of samples (a) Untreated (b) Laser fluence = 113.33 J/cm², Nitrogen flow rate = 15 l/min (c) Laser fluence = 84.88 J/cm², Nitrogen flow rate = 15 l/min (d) Laser fluence = 84.88 J/cm², Nitrogen flow rate = 25 l/min



Figure 5.3 Cross sectional SEM micrograph consisting of compound and diffusion layer

The cross-sectional microstructure taken on 1000 times magnification and on a scale of 10 μ m obtained after laser nitriding process is given in Figure 5.3. The nitride layer obtained consisted of two sub layers which are the compound layer and the diffusion layer. The average thickness of the compound layer was found to be ~13 to 15 μ m. The compound layer which is also called the white layer is rich in ε -nitride and appears feathery in structure. This layer acts a barrier against corrosion attack as well as it improves the tribological properties of the surface. These properties are attributed to the closely packed hexagonal ε -nitride present in this layer. According to the literature, ideally this layer should be free from pores, however in the obtained SEM images, a few horizontal microcracks were visible in the sample treated at higher fluences. For the sample treated at laser fluence = 84.88 J/cm² with nitrogen flow = 15 l/min, the appearance of this layer was smooth and free from pores. Hence, we can conclude that the formation of compound layer is affected by the laser parameters. Beneath the compound layer, diffusion layer was found. The average thickness of the diffusion layer was found to be ~ 30 to 32 μ m. The diffusion layer or diffusion zone consisted of precipitates of nitrides, iron and

other metals in the martensitic matrix. These precipitates distort the lattice and pin crystal dislocations and thereby increase the hardness of the surface layer. The diffusion layer predominantly determines the hardness of the nitrided surfaces.

5.2 Centerline Average Surface roughness

The centerline average value of surface roughness was calculated as an average of at least 10 successive measurements. The centerline average surface roughness values obtained after the laser nitriding process is shown in Table 5.2. The profilometry of the nitrided samples obtained on the computer is shown in Figure 5.4. The average roughness values of the samples increased from $\sim 90 \,\mu\text{m}$ to $\sim 60 \,\mu\text{m}$. During the nitriding process, as the laser beam falls over the sample surface, the material from that spot melts and gets removed from the center of the laser spot and falls out, and the piston effect and convection take place. All these processes together lead to macroscopic material transport and hence roughening of the surface.



Figure 5.4 Profilometry of samples on computer (a) Untreated (b) Laser fluence = 113.33 J/cm², Nitrogen flow rate = 15 l/min (c) Laser fluence = 84.88 J/cm², Nitrogen flow rate = 15 l/min (d) Laser fluence = 84.88 J/cm², Nitrogen flow rate = 25 l/min

S.No	Type of sample	Centerline average	
		Roughness value (Ra)	
		(μ m)	
1	Untreated Sample	~0.68	
2	Fluence = 113.18 J/cm ² , Nitrogen flow = 15 l/min	~ 0.903	
3	Fluence = 84.88J/cm ² , Nitrogen Flow = 15 l/min	~ 0.95	
4	Fluence = 84.88 J/cm ² , Nitrogen Flow = 25 l/min	~0.98	

Table 5.2 Centreline Average Surface Roughness value of laser nitrided sample

5.3 X- Ray diffraction Analysis:

Figure 5.5 depicts the X-ray diffraction pattern of the laser nitrided and untreated samples. The peak represents the (1 1 0) plane of the α -Fe phase at 44.78 in all spectra. In the laser nitride samples, there are also additional peaks at 42.3-43.2 and approximately 51.48, indicating the development of nitride or any other carbonitride phases, such as the hexagonal ε -Fe₂₋₃(N, C) phase and cubic γ -phase, also known as "nitrogen austenite". The iron atoms in the γ -phase are arranged in a face-centred cubic pattern, and nitrogen is filling the octahedral interstitial sites randomly and partly here. There is also an additional unindexed peak at about 41.88, representing the creation of some other carbonitride phases. It is also concluded from all the diffraction patterns that for the sample with a fluence of 84.88 J/cm² and nitrogen flow of 15 l/min, the peak indicating nitrogen austenite is higher than the other micrographs. Hence the parameters used in these samples are found to be optimum for the nitriding process. This analysis is also supported by SEM and EDAX results for the laser nitride samples. Hence XRD shows the formation of different nitride phases post laser nitriding process.



Figure 5.5 X-ray diffraction micrograph of untreated and laser nitrided sample

5.4 Microhardness

The microhardness values obtained after performing the laser nitriding with different fluences are shown in Table 5.3. Averages of at least 10 consecutive measurements on a 2N load were used to calculate the average hardness value for the untreated sample, and it was discovered to be 873 HV. The optimum hardness value for the laser nitride samples was found to be ~1247 HV for the sample with a nitrogen flow rate of 15 l/min and laser fluence of 84.88 J/cm². Here an increase of 42% in the hardness values compared to the untreated sample. During the nitriding process, precipitates of iron, nitride and other metals are formed on the grain boundaries inside the diffusion layer. These precipitates distort the lattice and pin crystal dislocations thereby raise the hardness of the surface. Also, the carbides formed in the martensitic matrix are made up of vanadium, tungsten, and molybdenum, providing higher hardness to high-speed steels. Hence the increased hardness value after the laser nitriding

process is attributed to the formation of carbides and various iron and nitride precipitates as well as to the introduction of various internal and thermal stresses in the sample.

S.No	Type of sample	Av. Microhardness	
		value (HV)	
1	Untreated Sample	~873 HV	
2	Fluence = 113.18 J/cm^2 , Nitrogen flow = 15 l/min	~856 HV	
3	Fluence = 84.88J/cm ² , Nitrogen Flow = 15 l/min	~1247 HV	
4	Fluence = 84.88 J/cm ² , Nitrogen Flow = 25 l/min	~1050 HV	

Table 5.3 Average Microhardness value of laser nitrided sample

5.5 Wear Analysis





Figure 5.6 Plots of coefficient of friction versus number of cycles for the samples (a) Untreated (b) Laser fluence = 113.33 J/cm², nitrogen flow rate = 15 l/min (c) Laser fluence = 84.88 J/cm², nitrogen flow rate = 15 l/min (d) Laser fluence = 84.88 J/cm², nitrogen flow rate = 25 l/min

The profiles of coefficients of friction of the untreated and laser nitride samples are shown in Figure 5.6. A relatively higher coefficient of friction was obtained for untreated samples. The average value of coefficient of friction for the untreated samples was found to be 0.31. A stick slip behavior in friction coefficient was also observed due to its lower value of hardness. When the surface of untreated HSS sample and the metallic counter body came in contact with each other, because of adhesion, one surface got stick to the another at the point of contact. Due to this, movement of the surface became difficult and hence the coefficient of friction was increased in the wear test of untreated samples. Tangential force led to the breakage of adhesive bonds at the interface, and it also led to fracture with decrease in the frictional force. As long as the wear test continued, the process of adhesion, breaking of adhesive bonds and fracture was being repeated.

For the laser nitrided samples, the values of coefficients of friction were found to be in the range of 0.17 to 0.20. This value is 45% lesser than those obtained for the untreated samples.

The reason behind this decrement in the values could be the lubricity of the compound layer which plays an important role in suppression of dynamic effects of friction. The ε -nitride phase produced on the sample surface has lamellar hexagonal close packed microstructure which allows smooth sliding along the base plane, reducing heat and friction produced. The non-metallic nature of ε -nitride phase reduces adhesion on metallic counterpart body and hence, reduces the adhesive component of coefficient of friction.

S.No	Type of sample	Av. wear volume (mm ³)	
1	Untreated sample	0.0017	
2	Fluence = 113.18 J/cm^2 , Nitrogen flow = 15 l/min	0.0030	
3	Fluence = 84.88 J/cm ² , Nitrogen flow = 15 l/min	0.0007	
4	Fluence = 84.88 J/cm^2 , Nitrogen flow = 25 l/min	0.0015	
	C C		

Table 5.4 Average wear volume of laser nitrided sample





b

а



Figure 5.7 Surface morphology of the wear track of the samples (a) Untreated (b) Laser fluence = 113.33 J/cm², nitrogen flow rate = 15 l/min (c) Laser fluence = 84.88 J/cm², nitrogen flow rate = 15 l/min (d) Laser fluence = 84.88 J/cm², nitrogen flow rate = 25 l/min



Figure 5.8 Electron dispersive spectroscopy graphs of the wear track of the samples (a) Untreated (b) Laser fluence = 113.33 J/cm², nitrogen flow rate = 15 l/min (c) Laser fluence = 84.88 J/cm², nitrogen flow rate = 15 l/min (d) Laser fluence = 84.88 J/cm², nitrogen flow rate = 25 l/min

The surface morphology of the wear tracks of the untreated and laser nitrided samples are shown in Figure 5.7. The micrographs were magnified 1000 times on a scale of 10 µm. After testing for a duration of 15 minutes, the characteristics of the worn surfaces of the untreated and laser nitrided samples revealed different wear behaviors. Severe metallic wear was observed in the untreated sample. Heavily scored surfaces along with metallic wear debris were observed. Adhesion and abrasion were the dominant mechanisms in this wear process. As the wear test was a ball on disk wear test, the contact stress led to asperity fracture between the ball (metallic counter body) and the sample and it facilitated abrasive and adhesive wear as the sliding distance increased. Therefore, the wear rate of the untreated sample was found to be greater than that of the laser nitrided samples. On the other hand, on the worn surface of the laser nitrided samples, mild abrasive wear can be observed after laser nitriding. The compound layer with high stress would fracture then it will transform into abrasive particles. Thus, in this case, as the sliding distance increased, adhesive wear diminished and abrasive wear became the dominant mechanism. As sliding distance increased further, the metallic counterpart came into contact with the diffusion layer. Due to the presence of the super saturated nitrogen, high amount of block carbides, as well various precipitates in this diffusion zone, extremally high compressive residual stresses were introduced in the diffusion layer. These compressive residual stresses would tend to close the existing microcracks, thus reducing the formation of wear particle which could have been produced by tensile stresses. Therefore, under this condition, the wear rate of the laser nitrided samples was still less than that of untreated samples even after the fracture of the compound layer.

Table 5.5 displays the predicted wear volume of the laser nitride samples. After the laser nitriding procedure, it was discovered that the wear volume of the sample had lowered by 53%. The electron dispersive spectroscopy micrographs are shown in Figure 5.8. After the analysis of the worn-out surface and the wear scars in the scanning electron microscopy micrographs,

it was concluded that the wear mechanism is mainly adhesion and abrasion. After laser nitriding, the amount of carbide was found to be increased. As far as high-speed steels are taken into consideration, their wear resistance generally depends upon the value of hardness and also on the nature, amount, distribution, and size of the carbides. As a general rule, high-speed steel has significant wear resistance as its hardness value increases. It is also observed that increasing the wear resistance of high-speed steels depends significantly more on the overall amount of the solid carbide phase. It is worthy to note that an increase in the volume amount of the solid carbides in the microstructure of high-speed steel is to be followed by an increase in its resistance to wear. As for the impact of the mode of carbide phase distribution on the wear resistance, it is revealed that eutectic carbides, which are located as nets within the boundaries of metal base grains, provide the best results. A large number of carbides can more effectively protect the steel matrix from wear than small ones. Hence the increase in the wear resistance can be attributed to the increased hardness, which in turn can be attributed to an increased number of carbides.

5.6. Economic Analysis:

As the author tried to analyze the process from economic point of view, it was found that if the rough cost of processing is calculated per sample, then it would be somewhere around INR 145. Here in this calculation, the author is assuming the cost of utilizing the laser facility to be INR 1000 per hour, the cost of liquid nitrogen to be INR 50 per liter, and cost of electricity consumption be INR 10 per unit. Hence, according to data of the experiment, it was assumed that the laser facility was used for 10 hours, approximately 35 liters of nitrogen was used in the processing of 100 samples, and approximately 100 units of electricity were utilized. According to this calculation, the cost of processing a single sample comes out to be INR 145. If we compare it with the cost of processing with plasma nitriding process, since plasma nitriding is the most efficient process after laser nitriding, then the let's assume the cost of utilizing the

laser facility is INR 1000 per hour and the cost of electricity is INR 10 per unit. Here, the cost of nitriding chamber will also be added in the processing cost, which is around 7 to 15 lacks according to the internet sources. Hence, the process of laser nitriding without the nitriding chamber will always remain economic in comparison to any process which requires nitriding chamber. Still, it was observed that a lot of gas gets wasted during the process so the author will try to think of economic ways of using liquid nitrogen so that the process could become more beneficial from the economic point of view.

Chapter VI: Conclusion

The open atmosphere laser nitriding of high-speed steel with varying fluences and varying nitrogen flow was successfully performed in this research work. The author used the novel technique, which is much easier and practically applicable in the present industry. From this research work, the following conclusions can be drawn:

(i) The novel process of laser nitriding in open atmosphere nitrogen performed in this research work for the first time is a promising method to improve the mechanical properties of highspeed steel.

(ii) Laser nitriding leads to microstructural changes in high-speed steel. The process leads to the inclusion of nitrogen in the form of nitride layer and an increased number of blocky carbides in the microstructure, which is responsible for the changes in mechanical properties.

(iii) Laser parameters and nitrogen flow rate significantly impact the microstructural and mechanical properties of laser nitride high-speed steel. Applying higher fluences and high nitrogen flow rate results in decreased hardness, increased surface roughness, and low wear resistance.

(iv) Higher hardness and wear resistance obtained by the process can be attributed to the increased number of carbides. A large amount of carbide can effectively protect the matrix from wear.

Appendix



Figure 1.1 Scanning electron microscopy setup



Figure 1.2 X- Ray Diffraction setup



Figure 1.3 Non-contact type surface profilometer



Figure 1.4 Vickers microhardness Tester



Figure 1.5 Fretting wear tribometer

References

- S. Šolić, Z. Schauperl, M. Godec, and V. Tropša, "Microstructural Changes in Heat Treatment of Pm High-Speed Steels," *Technical Journal*, vol. 11, pp. 166–170, 2017, [Online]. Available: https://www.researchgate.net/publication/340871321.
- [2] A. S. Chaus, "On the wear resistance of high-speed steels," *Journal of Friction and Wear*, vol. 29, no. 1, pp. 24–34, 2008, doi: 10.3103/s1068366608010054.
- [3] A. M. Bayer, B. A. Becherer, and T. Vasco, "Bulletin: High Speed Tool Steels," *Latrobe Specialty Steel Co.*, vol. 16, pp. 10–11.
- [4] O. Article, "Increasing tool life in machining of difficult-to-cut materials using nonconventional turning processes," *The International Journal of Advanced Manufacturing Technology*. pp. 1993–2004, 2015, doi: 10.1007/s00170-014-6588-7.
- [5] P. Beer, J. Rudnicki, S. Bugliosi, A. Sokołowska, and E. Wnukowski, "Low temperature ion nitriding of the cutting knives made of HSS," *Surface and Coatings Technology* vol. 200, no. 1-4 SPEC. ISS., pp. 146–148, 2005, doi: 10.1016/j.surfcoat.2005.02.031.
- [6] J. Nickel, A. N. Shuaib, B. S. Yilbas, and S. M. Nizam, "Evaluation of the wear of plasma-nitrided and TiN-coated HSS drills using conventional and Micro-PIXE techniques," *Wear*, vol. 239, no. 2, pp. 155–167, 2000, doi: 10.1016/S0043-1648(99)00352-X.
- [7] C. J. Copola "Influence of laser parameters on the nitriding of low carbon steel,"
 Applied Surface Engineering., vol. 197–198, pp. 896–903, 2002, doi: 10.1016/S0169-4332(02)00452-X.
- [8] C. K. Kim, J. Il Park, S. Lee, Y. Chan Kim, N. J. Kim, and J. Seung Yang, "Effects of

alloying elements on microstructure, hardness, and fracture toughness of centrifugally cast high-speed steel rolls," *Metallurgical and Materials Transaction. A Physical Metallurgy and Material Science.*, vol. 36 A, no. 1, pp. 87–97, 2005, doi: 10.1007/s11661-005-0141-0.

- [9] V. Arumugaprabu, T. J. Ko, S. Thirumalai Kumaran, R. Kurniawan, and M.
 Uthayakumar, "A brief review on importance of surface texturing in materials to improve the tribological performance," *Reviews on Advanced Material Science.*, vol. 53, no. 1, pp. 40–48, 2018, doi: 10.1515/rams-2018-0003.
- [10] A. E. A. Zeghni, "The effect of thin film coatings and nitriding on the mechanical properties and wear resistance of tool steel," *Journal of Materials and Processing Technology*, pp. 1–171, 2003.
- [11] S. Ghosh, Chetan, and P. V Rao, "Environment Friendly Machining of Ni Cr Co Based Super Alloy using Different Sustainable Techniques Environment Friendly Machining of Ni – Cr – Co Based Super Alloy using Different Sustainable Techniques," *Lunar Mapping and Modelling Project*, vol. 31, no. 7, pp. 852–859, 2016, doi: 10.1080/10426914.2015.1037913.
- [12] A. A. Khan and M. I. Ahmed, "Improving tool life using cryogenic cooling," *The Journal of Materials and Processing Technology.*, vol. 196, no. 1–3, pp. 149–154, 2008, doi: 10.1016/j.jmatprotec.2007.05.030.
- [13] K. N. Prasad and I. Syed, "Surface Texturing and Laser Shock Peening Processes on High-Speed Steel Tool for Sustainable Machining," *Arabian Journal for Science and Engineering*, 2021, doi: 10.1007/s13369-021-06367-z.
- [14] M. Dai, C. Li, and J. Hu, "The enhancement effect and kinetics of rare earth assisted salt bath nitriding," *Journal of Alloys and Compounds.*, vol. 688, pp. 350–356, 2016,
doi: 10.1016/j.jallcom.2016.07.189.

- [15] P. Schaaf, "Laser Nitriding in Materials," *Progress in Material Science*, vol. 47, pp. 1–161, 2002.
- [16] P. Schaaf, "Iron nitrides and laser nitriding of steel," *Hyperfine Interaction*, vol. 111, no. 1–4, pp. 113–119, 1998.
- [17] A. R. Kulkarni., "Influence of laser-nitriding on mechanical and elevated temperature fretting wear behavior of A356-alloy," *Surface and Coatings Technology*, vol. 413, no. March, p. 127072, 2021, doi: 10.1016/j.surfcoat.2021.127072.
- [18] E. D. Doyle., "Nitriding of high-speed steel," *International Heat Treatment and Surface Engineering*, vol. 5, no. 2, pp. 69–72, 2011, doi: 10.1179/174951411X12956208225348.
- [19] D. G. Fantineli, C. T. Parcianello, T. S. Rosendo, A. Reguly, and M. D. Tier, "Effect of heat and cryogenic treatment on wear and toughness of HSS AISI M2," *Journal of Materials Research and Technology.*, vol. 9, no. 6, pp. 12354–12363, 2020, doi: 10.1016/j.jmrt.2020.08.090.
- [20] H. Wang, R. Nett, E. L. Gurevich, and A. Ostendorf, "The effect of laser nitriding on surface characteristics and wear resistance of niti alloy with low power fiber laser," *Applied Science.*, vol. 11, no. 2, pp. 1–10, 2021, doi: 10.3390/app11020515.
- [21] M. Godec, Donik, A. Kocijan, B. Podgornik, and D. A. Skobir Balantič, "Effect of post-treated low-temperature plasma nitriding on the wear and corrosion resistance of 316L stainless steel manufactured by laser powder-bed fusion," *Additive Manufacturing.*, vol. 32, no. December, 2020, doi: 10.1016/j.addma.2019.101000.
- [22] V. Goyal, S. K. Sharma, and B. V. M. Kumar, "Effect of Lubrication on Tribological Behavior of Martensitic Stainless Steel," *Materials Today Proceedings.*, vol. 2, no.

4-5, pp. 1082-1091, 2015, doi: 10.1016/j.matpr.2015.07.013.

- [23] R. K. Singh Yadav, V. Sharma, and B. Venkata Manoj Kumar, "On the role of sliding load and heat input conditions in friction stir processing on tribology of aluminum alloy–alumina surface composites," *Tribology Materials. Surfaces and Interfaces*, vol. 13, no. 2, pp. 88–101, 2019, doi: 10.1080/17515831.2019.1591085.
- Y. S. Tian, C. Z. Chen, S. T. Li, and Q. H. Huo, "Research progress on laser surface modification of titanium alloys," *Applied Surface Science.*, vol. 242, no. 1–2, pp. 177–184, 2005, doi: 10.1016/j.apsusc.2004.08.011.
- [25] K. A. Rao, "Enhancing the Mechanical and Tribological Properties of Aluminum Alloys Through Alloying Addition and Laser-Assisted Surface Modification," Dspace, IIT Indore, November, 2021.
- [26] R. Aghababaei, D. H. Warner, and J. F. Molinari, "Critical length scale controls adhesive wear mechanisms," *Nature Communications.*, vol. 7, no. May, pp. 1–8, 2016, doi: 10.1038/ncomms11816.
- [27] S. Gupta, S. K. Sharma, B. V. M. Kumar, and Y. W. Kim, "Tribological characteristics of SiC ceramics sintered with a small amount of yttria," *Ceramics International*, vol. 41, no. 10, pp. 14780–14789, 2015, doi: 10.1016/j.ceramint.2015.07.210.
- [28] S. K. Sharma, B. V. M. Kumar, and Y. W. Kim, "Effect of WC addition on sliding wear behavior of SiC ceramics," *Ceramics International*, vol. 41, no. 3, pp. 3427– 3437, 2015, doi: 10.1016/j.ceramint.2014.10.144.
- [29] R. Manoj Kumar, S. K. Sharma, B. V. Manoj Kumar, and D. Lahiri, "Effects of carbon nanotube aspect ratio on strengthening and tribological behavior of ultra-high molecular weight polyethylene composite," *Composites Part A: Applied Science and*

Manufacturing, vol. 76, pp. 62–72, 2015, doi: 10.1016/j.compositesa.2015.05.007.

- [30] S. K. Sharma, B. Venkata Manoj Kumar, K. Y. Lim, Y. W. Kim, and S. K. Nath, "Erosion behavior of SiC-WC composites," *Ceramics International*, vol. 40, no. 5, pp.6829–6839, 2014, doi: 10.1016/j.ceramint.2013.11.146.
- [31] R. Veinthal, F. Sergejev, A. Zikin, R. Tarbe, and J. Hornung, "Abrasive impact wear and surface fatigue wear behavior of Fe-Cr-C PTA overlays," *Wear*, vol. 301, no. 1–2, pp. 102–108, 2013, doi: 10.1016/j.wear.2013.01.077.
- [32] R. Manoj Kumar., "Electrophoretic deposition of hydroxyapatite coating on Mg-3Zn alloy for orthopedic application," *Surface and Coatings Technology.*, vol. 287, pp. 82–92, 2016, doi: 10.1016/j.surfcoat.2015.12.086.
- [33] S. Q. Wang, M. X. Wei, F. Wang, and Y. T. Zhao, "Transition of elevated-temperature wear mechanisms and the oxidative delamination wear in hot-working die steels," *Tribology International*, vol. 43, no. 3, pp. 577–584, 2010, doi: 10.1016/j.triboint.2009.09.006.
- [34] J. Fernández-Pérez, J. Díaz-Álvarez, M. H. Miguélez, and J. L. Cantero, "Combined analysis of wear mechanisms and delamination in CFRP drilling," *Composite Structures*, vol. 255, no. March 2020, doi: 10.1016/j.compstruct.2020.112774.
- [35] N. P. Suh, "The delamination theory of wear," *Wear*, vol. 25, no. 1, pp. 111–124, 1973, doi: 10.1016/0043-1648(73)90125-7.
- [36] W. Shin., "Surface & Coatings Technology Microstructural characterizations and wear and corrosion behaviors of laser-nitrided NAK80 mold steel," *Surface and Coatings Technology*, vol. 410, no. January, psp. 126956, 2021, doi: 10.1016/j.surfcoat.2021.126956.

- [37] G. Yan., "Wear and corrosion behavior of P20 steel surface modified by gas nitriding with laser surface engineering," *Applied Surface Science*, vol. 530, no. July, p. 147306, 2020, doi: 10.1016/j.apsusc.2020.147306.
- [38] P. P. Psyllaki, A. Griniari, and D. I. Pantelis, "Parametric study on laser nitriding of 1.5919 steel," *Journal of Materials and Processing Technology*, vol. 195, no. 1–3, pp.299–304, 2008, doi: 10.1016/j.jmatprotec.2007.05.023.
- [39] M. Kulka, D. Panfil, J. Michalski, and P. Wach, "The effects of laser surface modification on the microstructure and properties of gas-nitrided 42CrMo4 steel," *Optics and Laser Technology*, vol. 82, pp. 203–219, Aug. 2016, doi: 10.1016/J.OPTLASTEC.2016.02.021.
- [40] A. Sim, C. Park, N. Kang, Y. Kim, and E. J. Chun, "Effect of laser-assisted nitriding with a high-power diode laser on surface hardening of aluminum-containing martensitic steel," *Optics and Laser Technology*, vol. 116, no. December 2018, pp. 305–314, 2019, doi: 10.1016/j.optlastec.2019.03.040.
- [41] B. S. Yilbas, A. F. M. Arif, C. Karatas, S. Akhtar, and B. J. A. Aleem, "Laser nitriding of tool steel: Thermal stress analysis," *International Journal of Advanced Manufacturing Technology*, vol. 49, no. 9–12, pp. 1009–1018, 2010, doi: 10.1007/s00170-009-2467-z.
- [42] P. Aisi, W. S. Shin, "Effect of Laser Heat-Treatment and Laser Nitriding on the MicrostructuralEvolutions and Wear Behaviors of Steels" *Metals*, 2020
- [43] R. Jendrzejewski, G. Sliwinski, I. Martev, N. N. Nedialkov, and P. A. Atanasov,
 "Laser treatment of the 38HMJ steel surface in a liquid nitrogen environment," *Laser Technology VI Applied Vol.* 4238, p. 149, 2000, doi: 10.1117/12.405970.

- [44] E. Boztepe, A. C. Alves, E. Ariza, L. A. Rocha, N. Cansever, and F. Toptan, "A comparative investigation of the corrosion and tribocorrosion behavior of nitrocarburized, gas nitrided, fluidized-bed nitrided, and plasma nitrided plastic mould steel," *Surface and Coatings Technology*, vol. 334, pp. 116–123, 2018, doi: 10.1016/j.surfcoat.2017.11.033.
- [45] S. Jan, "Wear and corrosion resistance of a plasma-nitrided PM tool steel alloyed with niobium ` era," *Surface and Coatings Technology*, vol. 200, pp. 5229–5236, 2006, doi: 10.1016/j.surfcoat.2005.06.023.
- [46] D. C. Wen, "Plasma nitriding of plastic mold steel to increase wear- and corrosion properties," *Surface and Coatings Technology*, vol. 204, no. 4, pp. 511–519, 2009, doi: 10.1016/j.surfcoat.2009.08.023.
- [47] P. Taylor, U. K. Mudali, H. S. Khatak, B. Raj, and M. Uhlemann, "Surface Alloying of Nitrogen to Improve Corrosion Resistance of Steels and Stainless Steels" *Materials and Manufacturing Processes*, December 2014, pp. 37–41, doi: 10.1081/AMP-120027501.
- [48] M. A. Obeidi, E. Mccarthy, and D. Brabazon, "Laser surface processing with controlled nitrogen-argon concentration levels for regulated surface life time," vol. 102, *Optics and Lasers in Engineering*, no. August 2017, pp. 154–160, 2018, doi: 10.1016/j.optlaseng.2017.11.007.
- [49] D. Höche, J. Kaspar, and P. Schaaf, "Laser nitriding and carburization of materials," *Laser Surface Engineering Processes and Applications*, pp. 33–58, 2015, doi: 10.1016/B978-1-78242-074-3.00002-7.