Chapter 2
High Temperature Tribology of Surface Coatings

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1 Introduction

Coating is deposited onto a substrate to modify it surface properties. The coating deposited is generally protective in nature and improves surface finish, wear resistance, scratch resistance, corrosion resistance, hardness, etc. Thus, a thin layer of a coating effectively improves surface properties without the need to alter the bulk properties of a material. Surface coatings may be soft or hard with anti-friction and anti-wear characteristics, respectively [50]. Nevertheless, the coatings may also be typically classified according to their deposition techniques [47]. The classification of coatings based according to their deposition techniques is presented in Fig. 1.

Hard surface coatings are used for improving wear resistance of the substrates and enhancing tribological behavior of mating parts in cylinder liners, piston rings, etc. Hard ceramic coatings are used in bearings and seals operating in extreme conditions, slurry pump seals, valves, knife sharpeners, gas turbine blades, etc. [50]. In various industries, several mating components are exposed to high temperature sliding conditions and environments. Generally, the interfaces of various moving assemblies in automotive, power generation, aerospace as well as metal working process involve high temperature mating components. High temperature exposure leads to morphological as well as microstructural changes due to enhancement of reactions and various other interactions of parameters. The mechanical properties of the materials are also affected due to oxidation and diffusion phenomenon. Thus, the synergistic effect of these entire phenomena affects the friction and wear behavior of materials
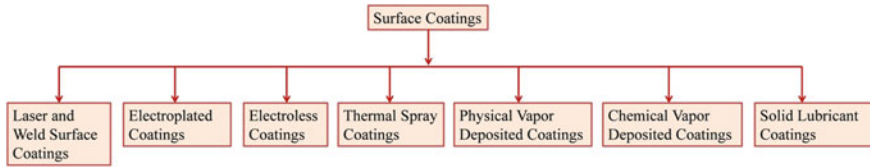
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Fig. 1 General classification of coatings [47]. Reprinted from Encyclopedia of Tribology, In: Wang Q.J., Chung YW. (eds), Caroline Richard, Tribological coatings for high temperature applications, 2013, with permission from Springer

at high temperature. Recent developments have seen mono- or multi-layered coatings with several functionalities that prevent components from degradation due to friction, wear, or corrosion. Tribo-corrosion, i.e., the synergy of tribology as well as corrosion phenomenon also magnifies degradation of mating components. In such cases, modern coatings have been successfully utilized. For high temperature applications, where conventional lubricants fail, suitable surface modification and surface coatings find usage [47]. It is desirable that these coatings should have high thermal stability and capability of providing self-lubrication. Super hard materials and nano-composites referred to as diamond or diamond-like-carbon coatings are finding increasing usage [47]. The thermal stability as well as tribological characteristics may be improved by deposition of multi-layered coatings thus combining individual properties of various coatings. Deposition of poly-alloyed coatings also serves the purpose of achieving a wide range of enhanced characteristics and mechanical properties for use in the high temperature domain. Electrodeposition and electroless nickel coatings also provide superior wear resistance at elevated temperatures [38].

Surface coatings are gaining significant importance in the high temperature domain. Some typical examples of the high temperature industrial applications include metal processing, automotive, and aerospace industries. Hot drawing is extensively used in the automotive industry for manufacturing parts like bumpers, door beams, hood reinforcements, etc. Friction and wear of tool occur during dry contact of the tools with sheet. The hot drawing process may be optimized by the use of high temperature coatings which will in turn reduce manufacturing costs [47]. Further, thermal barrier coatings are effective in reducing losses arising due to oxidation and wear of vanes of gas turbine or aero-engines and highly loaded turbine blades [47]. Researchers have also shown that thermal sprayed coatings may be successfully used in aerospace, mining, and automotive industries [41, 55]. Plasma-sprayed PS series coatings developed at National Aeronautics and Space Administration (NASA) were also seen to be efficient over a broad operating temperature range and it was concluded that PS400 series coatings were suitable for aerospace applications [48]. Recent studies have also shown that electroless deposited alloy coatings have enhanced tribological characteristics at high temperatures of 500 °C [36].

Therefore, with rising industrial demands and harsh environments, there is a need to study different coating methods which have been explored by researchers for the high temperature domain. The present chapter aims to provide a concise discussion

on high temperature-based coating design and deposition techniques. Recent developments and future trends are also discussed with an aim to enhance the surface engineering techniques for high temperature-based tribological applications.

2 Surface Coating Deposition Techniques

Surface engineering has gained immense importance since components are subjected to various surface attacks in the form of friction, wear, and corrosion. Automotive, aviation, power, chemical, etc., industries depend heavily on surface engineering and coatings. To meet demanding needs and cater into leading-edge technology, it is necessary to optimize both volumes of components as well as surface properties. There are several methods of coating deposition. The properties of the coatings depend on the process chosen. Further, the parameters of coating deposition in a certain process also control the friction, wear, and corrosion resistance of the coatings [7]. A coating process is also selected based on environmental condition, loading, operating temperature, cost effectiveness, etc. Right choice of coating material and process parameters would allow components working in severe environments to excel in high temperature conditions. Some techniques which are used for deposition of coatings related to high temperature applications are discussed subsequently.

2.1 Vapor Deposition Techniques

Vapor deposition technique refers to the deposition of a material which is in vapor state and condensed onto a substrate. In this method, ions, atoms, or molecules in gaseous phase are utilized to deposit coatings having excellent tribological characteristics. The process is versatile and produces coatings with high purity and adhesion to the substrate. They also replicate the surface of the substrate and there is no requirement of post finishing operations. Since vapor deposition takes place in a vacuum chamber, the cost of the system is comparatively higher. Vapor deposition may be broadly classified as:

- Physical vapor deposition (PVD)
- Chemical vapor deposition (CVD).

2.1.1 Physical Vapor Deposition (PVD)

In PVD, the starting material is in the form of a solid. As energy is introduced, the solid is transformed to gaseous or plasma phase [30]. High vacuum is used to condense the vapor (10^{-8} to 10^{-1} torr) on the substrate [50]. The steps involved in PVD include (a) generation of gaseous phase, (b) transport of particles, and (c) condensation and growth of layer [30]. The different ways by which coatings are
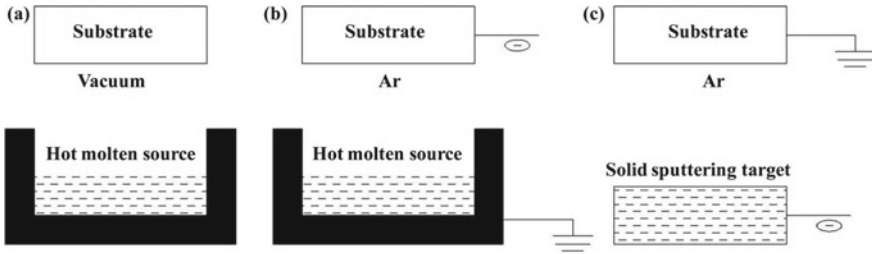
Fig. 2 Schematic diagram of PVD processes: **a** evaporation, **b** ion-plating and **c** sputtering

deposited by PVD for high temperature applications are mainly through arc PVD, sputtering, and ion-plating. The PVD process is shown schematically in Fig. 2. The different PVD processes are discussed in brief as follows:

Arc PVD: By this process, the solid metallic coating material is evaporated by running an arc having diameter of a few microns. Due to the high current, high energy plasma is formed and the material that is evaporated is almost totally ionized. A reactive gas is passed through the chamber wherein the metal ions combine with it and get deposited on the substrate or component. Thus, a thin and highly adherent coating is formed.

Sputtering: Sputtering is a widely used vapor deposition technique. The solid coating material is dislodged into the vapor phase due to bombardment of energetic particles and positive ions of heavy inert gas (argon ions). A negative voltage is applied to the target. Due to the applied negative voltage, the positive Ar ions are accelerated towards the target. The atoms or ions required for deposition are ejected by momentum transfer. The particles that are evaporated are finally introduced into a chamber with a gas containing the non-metallic component of the hard coating. Sputtering being a high energy process, any material may be deposited since the coating material is passed into the vapor phase by mechanical process.

Ion-plating: When the starting material is ionized in plasma, high energy ionized particles are yielded for coating deposition. This is known as ion-plating. To increase the adhesion of coating to the substrate, partial ionization of the vapor is carried out. Either the material to be deposited is passed through a gaseous glow discharge (plasma) or an external ionization gun is utilized as the bombardment source. Adhesion of ion beam-type coatings is found to be excellent even at low substrate temperature.

2.1.2 Chemical Vapor Deposition (CVD)

In CVD technique, the components in gaseous phase react close to or on the substrate to be coated [30]. A volatile component of the coating is reacted with gases or vapor or decomposed thermally on to the hot substrate [50].Chemical reaction is initiated at 150–2200 °C. The pressure is kept at 0.5–760 torr. The substrate is heated by

laser or a heater. Coatings with excellent quality and adhesion are produced by low pressure CVD with high deposition rate [50]. Since deposition at high temperature is involved in CVD, it limits the deposition on substrates with low melting point.

2.2   Electrodeposition

This is an electrochemical deposition process wherein a current is passed externally. This allows influence over direction in which the reaction proceeds and metal deposition [30]. current is passed through a solution called the electrolyte. Generally, DC current source is applied and at times, pulsed technique is employed. The pulsed process enables deposition of graded and multi-layer coatings. The dissolution of metal ion to be deposited takes place either by dissolution of anode or the electrolyte [30]. The material to be coated is cathode. Thus, reduction of metal ions takes place at the cathode. One of the pre-requisites is that the substrate must be electrically conductive. A variety of metals can be deposited by electrodeposition. The electrodeposition setup is presented schematically in Fig. 3.
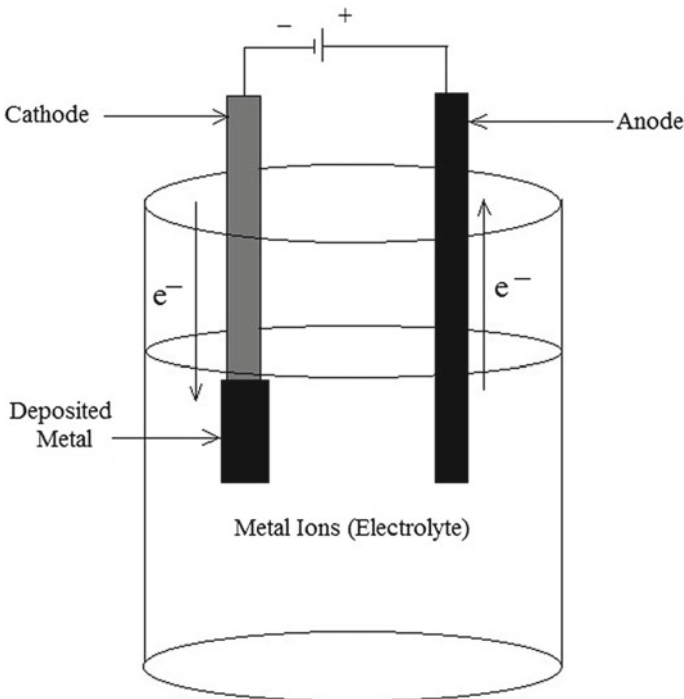

Fig. 3 Electrodeposition setup

2.3 Electroless Deposition

Electroless process is a chemical process and is also known as autocatalytic process. It takes place by autocatalytic chemical reduction. There is no aid of electricity to trigger reactions. The coating bath consists of a reducing agent. This reducing agent provides electrons to reduce metallic ions on to the substrate which must be catalytically active. Since it is not necessary that the substrate be electrically conducting, this process is flexible and a broad type of substrates can be plated easily. Even though electroless deposition is receiving widespread attention now, the reduction of nickel from its aqueous solution from a hypophosphite based bath was made by Wurtz [51]. Wurtz idea was not developed for a whole century until Brenner and Riddell [3] conducted the first laboratory experiment and were given the credit for introducing electroless nickel coating to the world. Basically, electroless nickel coatings may be classified as Ni–P- or Ni–B-based alloy and composite coatings. After receiving significant attention, it has grown into a wide family of functional coatings serving several industrial needs. The main application of electroless nickel is based on its corrosion resistance and anti-wear characteristics. The main disadvantage of this process is its finite bath life. The electroless nickel deposition process has been schematically depicted in Fig. 4.
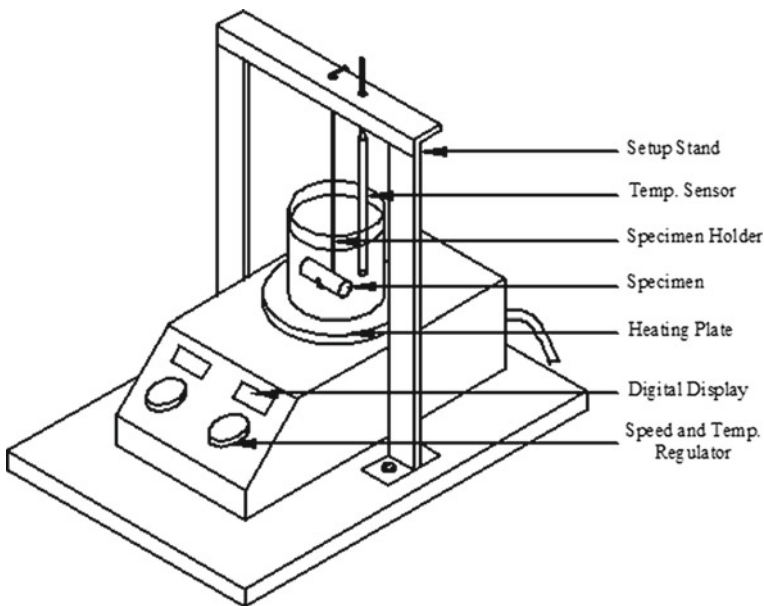

Fig. 4 Electroless nickel deposition setup

2.4 Hard Facing

Hard facing may be done by thermal spraying, welding, or cladding [50]. Thick and hard coatings are produced by hard facing. The coating is melted in a heating zone and sprayed on to a cooled substrate material. Thermal energy for melting the material is obtained by a flame, electric plasma, detonation of gases by a spark plug, etc. [50]. When coating material is supplied in the form of a powder, wire or rod and heat are produced by a gas, flame, or electric arc, and the process is known as welding deposition. In cladding, a metallic foil or sheet is metallurgically bonded to a metallic substrate. There are several methods by which a metal or alloy may be clad such as deformation cladding, braze cladding, diffusion bonding, weld cladding, and laser cladding. Plastic deformation applied through pressure/impact along with heat results in a true metallurgical bond and the process is known as deformation cladding. Diffusion bonding relies on the principle of coalescence of contacting surfaces by the application of pressure and heat for short time. When surfaces are sandwiched by a brazing material in the form of a paste, foil or powder, it is known as braze cladding. The stack is heated by a heat source to form metallurgical bond [50]. In weld and laser cladding, the metal is clad by melting it and fusing it to the substrate.

3 High Temperature Tribology of Coatings Deposited by Different Techniques

3.1 PVD/ Arc-PVD Coatings

Tribologically protective coatings were deposited onto tools and components by deposition of ions, atoms, or molecules in gaseous phase by PVD process [30]. Several research works regarding PVD for high temperature applications have been carried out. Nohava et al. [40] demonstrated the tribological behavior of Al–Cr-based wear-resistant coatings that are suitable for the high temperature domain (oxynitride and oxide coatings). An industrial rotating arc-cathode PVD process was used for coating deposition. High wear resistance was observed for AlCrN coatings up to 600 °C. But the coatings failed at 800 °C. Severe wear was exhibited by all nitride and oxynitride coatings at 800 °C. But α-$(Al,Cr)_2O_3$ coating exhibited outstanding wear resistance at 800 °C. This was attributed to its stable alpha-alumina structure. This hindered oxidation of the coating at high temperature and consequently a severe wear. It was concluded that not only the ability of the coating to prevent oxidation of the substrate but also its excellent abrasion resistance led to high wear resistance at 800 °C. $(Ti_{0.7}Al_{0.3})$ N coatings deposited by PVD process were also considered to be wear resistant at high temperatures [49]. Hence, these coatings were deposited on AISI H13 steel which is generally used as dies in hot extrusion. The wear resistance of the coatings was investigated at room temperature as well as at 600 °C. As-received and gas-nitrided coatings were considered. Different substrates, coatings,

Table 1 Nomenclatures of heat-treated AISI H13 steel substrates and coatings considered by Rodríguez-Baracaldo et al. [49]

Nomenclature	Cooling	Other treatments	Coating
HA	Air	–	–
HAN		Nitriding	–
HAB		–	TiAlN
HANB		Nitriding	TiAlN
HO	Oil quenched	–	–
HON		Nitriding	–
HOB		–	TiAlN
HONB		Nitriding	TiAlN

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and their nomenclature are shown in Table 1 while their COF and wear volume are presented in Table 2. The gas nitride coatings exhibited satisfactory wear resistance compared to bare steel or the as-deposited coatings. High load carrying capacity and H/E ratio were the reason behind excellent wear resistance which allowed the presence of higher elastic strain. Further oxidation of the coating was prevented by dense oxide formation in the wear track. Though it was reported by Nohava et al. [40] that $(Al,Cr)_2O_3$ coatings were more wear resistant than TiAlN coating variants.

The high temperature tribological behavior of Ti6Al4V was improved by nitriding and subsequent application of TiAlN coatings prepared by cathode arc-evaporation technique [39]. The test temperature was changed from 25 to 600 °C. Wear rate was observed to be lowest at 500 °C. The higher wear resistance was attributed to the tribochemical films of Al_2O_3 and TiO_2. Similar results were also observed for $Ti_{55}Al_{45}N$ and $Ti_{35}Al_{65}N$ nitride coatings prepared by cathode arc-evaporation technique [16].

Table 2 COF and wear volumes of AISI H13 steel (coated and non-coated) at room and high temperatures investigated by Rodríguez-Baracaldo et al. [49]

Temperature (°C)	Sample	COF	Wear volume (mm^3)
600	HA	0.55	0.083
600	HAN	0.6	0.015
600	HAB	0.65	0.054
600	HANB	0.95	–
600	HO	0.52	0.143
600	HON	0.60	0.017
600	HOB	0.67	0.030
600	HONB	0.93	–

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The wear resistance was significantly improved at 600 °C with an increase in Al. Zr–Si–N coatings was deposited by cathodic arc technique on WC–Co substrates [60]. The Si content was varied from 0.2 to 6.3 at.%. Consequently, there was a change in microstructure from columnar to nanocomposite. It was suggested that columnar-structured coatings and higher Si yields superior macro-scale wear resistance at room and elevated temperature (500 °C). Hot forging tools were seen to be efficiently protected by nitriding and PVD coating [13]. Hybrid layers of Cr/CrN/AlTiCrN coating, Cr/CrN coating, and CrN/AlCrN/AlCrTiSiN coating were applied on hot forging tool steel. Cr/CrN coatings were effective in protecting the tool steel from wear. This was attributed to its high adhesion and resistance to abrasion. Further, Cr/CrN/AlTiCrN coating was also effective in improving the lifetime of tool steel due to its high resistance to abrasion. It also formed a thermal barrier. This resulted in a limited heat transfer. The PVD process also includes sputtering and ion-plating and has been discussed subsequently.

3.1.1 Sputtered Coatings

TiN and CrN coatings were deposited by low voltage arc deposition technique. Further, TiCN was also deposited by magnetron sputtering. Their high temperature tribo-performance was examined [44]. Significant oxidation of the coatings was observed at temperatures above 300 °C when sliding against Si_3N_4 balls. Austenitic steel substrate coated with TiCN by unbalanced magnetron sputtering was also tested at different temperatures while sliding against 100Cr6 balls [45]. Plastic deformation was dominant for TiCN coatings below 200 °C while within 300–500 °C, the major wear mechanisms observed were fracture, delamination and oxidative. TiN coatings deposited by high impulse magnetron sputtering were seen to exhibit high wear resistance at 300 °C [24]. But above 450 °C, oxidation of the coating was unavoidable. Further at 600 °C, the coatings were oxidized and cracked easily. The COF decreased as test temperature increased as shown in Fig. 5. WS_x co-deposited along with TiN

Fig. 5 COF of high impulse magnetron sputtered TiN coatings at room and high temperature [24]. Reprinted from Coatings, 9, Kuo et al., High temperature wear behavior of titanium nitride coating deposited using high power impulse magnetron sputtering, 555, 2019
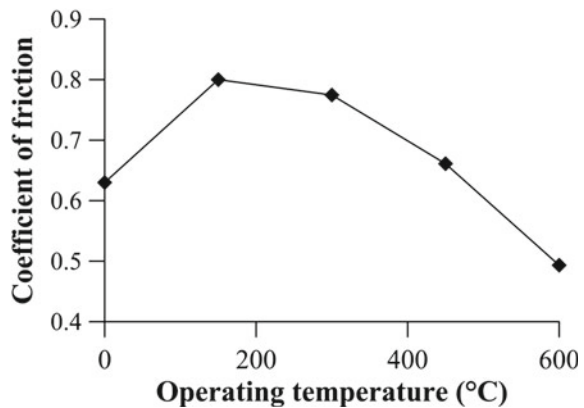
coatings by reactive magnetron sputtering was investigated by Serra et al. [52]. Coated specimens containing 4 at. % WS_x were not effective at 343 K and its properties deteriorated. But on increasing the WS_x content to 19 at. %, a low COF and optimum wear rate of 0.86×10^{-17} m^2/N was observed without any cracking.

Adaptive and friction reducing coatings were produced by unbalanced magnetron sputtering that consisted of niobium nitride with silver nano-inclusions [57]. Tribological tests at 25–1000 °C was carried out while sliding against Si_3N_4 counterface. Above 700 °C, the coefficient of friction (COF) was within 0.15–0.30. At lower temperatures, COF was low due to the migration of silver to the surface. On the other hand, at high temperature, lubricious glazes were formed and responsible for the reduction of COF. The coatings were further doped with MoS_2. A low temperature lubricant like MoS_2 was added to investigate its effect on tribological behavior at high temperature. There was no appreciable change in COF at room temperature on addition of MoS_2. The COF at high temperatures was appreciably lower due to synergy of lubricating effects of molybdates and silver niobates. Silver tantalate coatings produced by unbalanced magnetron sputtering were investigated at ~750 °C [56]. They exhibited COF in the range 0.06–0.15. Reconstruction of self-lubricating $AgTaO_3$ into a mechanically mixed layer (MML) comprising Ta_2O_5, $AgTaO_3$ and Ag nano-particles were attributed to this low COF. Furthermore, magnetron-sputtered VN/Ag coatings were found to be adaptive and self-lubricating at high temperatures [2]. The COF of the coatings was found to be in the range of 0.15–0.20 at 700–1000 °C. Analysis of wear tracks using EDX and XRD revealed silver vanadate, silver, and vanadium oxide formation. Due to the layered atomic structure of Ag_3VO_4 such low COF was observed.

For high temperature friction and wear resistance, magnetron-sputtered multi-layered CrAlN/VN coatings were deposited and investigated by Wang et al. [59]. Preferable anti-wear characteristics were observed at 700 °C. This was attributed to interfacial strengthening and the formation of lubricated vanadium oxide layers on the worn surface. The anti-wear property of the multi-layered coatings at high temperature was due to contribution of the respective elements and structural strengthening. Sputtered CrV_xN coatings with varying V content were studied by Rapoport et al. [46]. Their friction behavior at high temperature was also investigated. The stick–slip phenomenon was also observed. Experiments were performed from 25 to 700 °C under low sliding velocities. Experimental results revealed that with an increase in V up to 27–35 at.% resulted in an increase in hardness, fracture toughness, and a decrease in grain size. Consequently, the tribological behavior improved. Strong stick–slip was observed at room temperature due to mechanical interlocking as a result of adhesion. Lower wear and stick slip at high temperature was associated with formation of low shearing tribofilm of V_2O_5. DC magnetron-sputtered MoS_2 and $MoSe_2$ coatings were prepared [20]. Their tribological characteristics were measured at high temperature and in air with varying humidity levels. The high temperature tests were carried out on a ball-on-disc high tribometer. Results revealed that air humidity did not influence the COF of $MoSe_2$ [20].

3.1.2   Ion-Plated Coatings

High temperature tribological behavior and adhesion strength of ion-plated TiN coating with Ni–W interlayer was deposited [14]. The substrate considered was a hot work die steel. Crsytallization was observed during TiN deposition. The precipitation hardening of Ni–W interlayer was also reported. Considering the thermal aspects of the deposition, an interface diffusion layer was also formed. Precipitation hardening of the Ni–W interlayer resulted in an effective support of the TiN coating due to an increased toughness as well. The adhesion of TiN coating with Ni–W interlayer improved consequently. In comparison with single TiN coating, the duplex coating had a significantly higher wear resistance at 500–700 °C. The predominant wear mechanism at elevated temperature was abrasive and adhesive. The tribo-perfromance of AlTiN coating deposited by cathodic arc ion-plating was investigated at 700–900 °C [8]. Oxides of Al_2O_3 and TiO_2 were formed which provided a lubricating effect at high temperature. The average COF of the AlTiN coating was 0.77, 0.65, and 0.57 at 700 °C, 800 °C, and 900 °C, respectively. Oxidative, abrasive, fatigue, and adhesive wear were the predominant mechanism. Cathodic arc ion-plating was used to deposit VN and VCN coatings [32]. Lower COF and wear was exhibited by VCN coating compared to VN coating at different operating temperatures. Formation of a self-lubricating oxide of V_2O_5 and carbon phase indicated that the coating may be used for potential applications and tribo-components working under high temperature. Cathodic arc ion-plating was used to deposit CrN coatings on YT14 cemented carbide cutting tools [15]. At 3 N load, the high temperature friction and wear characteristics were excellent but at 7 N, the coatings failed. Abrasive, oxidative, adhesive, and plastic deformation was the dominant wear mechanisms. At 300, 400, and 500 °C, the COF of CrN coatings was 0.50, 0.62, and 0.43, respectively [53]. Abrasive wear was dominant at 300 and 400 °C. At 500 °C, slight oxidation along with abrasive wear was dominant.

3.2   CVD Coatings

CVD coatings have been investigated as potential candidates for high temperature extrusion process. H11 tool steel was surface engineered for aluminum extrusion dies. The tribological configuration involved sliding of 6082Al disc against die block at high temperatures [43]. Comparison of base steel and nitrided steel was carried out. Furthermore, deposition of commercially available duplex CVD and PVD coatings were considered. The ability of surface finish in influencing the tribo-performance was also investigated and no significant effect was concluded. Heavy damage was observed for the steel and nitride samples. Surface examination post wear tests revealed delamination pits and large craters in the sub-surface region. In the compound layer of coating, the hard duplex PVD coating was seen to be delaminated only in the outermost region. Compared with PVD, the bi-layered TiC-TiN CVD coating with lower load bearing capacity showed lesser damage. The influence

of temperature on the wear performance of CVD coating deposited on CoCrFeMnNi high entropy alloy (HEA) bonded Ti(C,N)-based cermets was studied by Chai et al. [4]. Five layers of CVD coating in the sequence TiN, MT-TiCN, transition layer (TiCO), α-Al$_2$O$_3$, and TiN were deposited. The substrate was HEA-bonded cermet. Wear test was carried out at 700 °C. Excellent wear resistance was observed compared to Ni-bonded cermet and this was attributed to small grain size, good adhesion, and hardness. Adhesive, abrasive, and oxidative wear was seen to be predominant.

3.3 Electrodeposited Coatings

Hot dip aluminized Zn–Ni coatings were electrodeposited on manganese boron flat steel. The hot forming application was simulated [19]. The tribo-performance of the coatings was investigated in the form of hot strip drawing and hot forming. Al-Si coatings were also considered. Higher COF was observed for Al-Si coatings compared to Zn-Ni coatings. This was attributed to the formation of a zinc oxide layer. The ZnO was also responsible for the enhancement of wear of work piece. Tribological characteristics of pure Ni coating and with micro/nanoSiC were observed at room as well as high temperature (300 °C) by Lekka et al. [26] under high load conditions. At room temperature, the wear resistance of pure Ni as well as with micro-SiC was almost similar. Inclusion of nanoSiC led to a 70% decrease in wear rate. All the coatings presented a higher wear rate at 300 °C due to lowering of mechanical strength and an increase in ductility of the matrix. But compared to pure Ni, the wear rate decreased by 63 and 88% on inclusion of micro-SiC and nano-SiC, respectively. The increased wear resistance of Ni-nano-SiC coatings was attributed to the uniform distribution of SiC throughout the deposit which inhibited plastic deformation. The wear mechanism at high temperature was observed to be tribo-oxidative and presence of micro-particles favored the mechanical adhesion of nickel oxide. Compared to DC current, pulsed current (PC) has the capability to produce lamellar structure and increase deposition of micro-SiC [25]. A clear grain refinement was observed when Ni-nano-SiC coatings were electrodeposited using PC. Compared to DC, the hardness of composite coatings improved when PC was applied. The wear mechanism at 300 °C was predominantly tribo-oxidation along with abrasion for the composite coatings.

Ni–SiC, Ni–SiC–MoS$_2$, and Ni–SiC–Gr composite coatings were fabricated by electrodeposition. This was done by a suspension of reinforcement particles well dispersed in a Ni sulfamate plating bath [9]. The COF of Ni–SiC coating was stable at room temperature. An increase in operating temperature resulted in a decrease in COF. At 100, 200, and 300 °C, the increase in COF was 17%, 80%, and 67%, respectively, compared to room temperature (25 °C). Wear surface examinations revealed spalling as the prevalent wear mechanism at various temperatures. At low temperature, the COF was smoother due to lower delamination. But the ductility of Ni matrix increased with an increase in temperature resulting in more plastic deformation. Addition of solid lubricating particles such as graphite or MoS$_2$ increased

Fig. 6 COF of electrodeposited Ni with inclusion of SiC, MoS₂, and Gr at different temperatures [9]. Reprinted from Surface and Coatings Technology, 254, Fazel et al., Effect of solid lubricant particles on room and elevated temperature tribological properties of Ni–SiC composite coating, 252–259, 2014, with permission from Elsevier
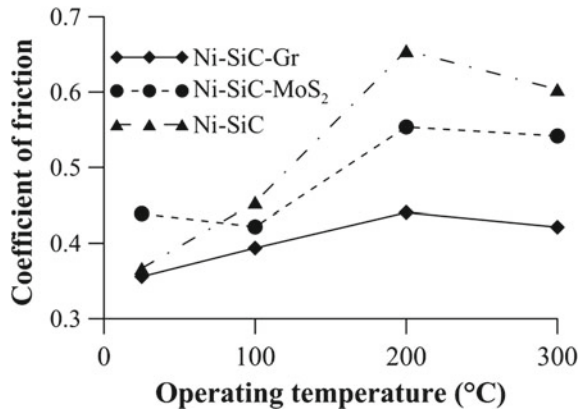
the stability of COF at high temperature. A consequent reduction of 10–15% in COF was seen. Strong adhesive wear was reduced on addition of graphite providing effective lubrication at high temperature. The reduction in COF was more than 30% for graphite containing coating at high temperatures as indicated in Fig. 6.
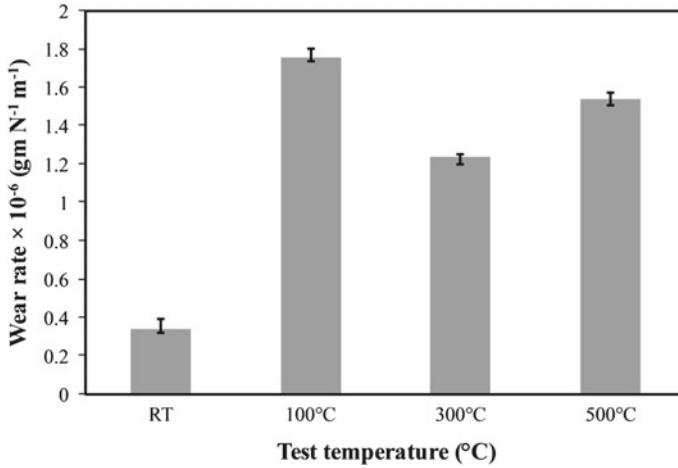
3.4   Electroless Deposited Coatings

Electroless deposited coatings have high hardness and enhanced tribological characteristics. They have proven self-lubricating nature and anti-wear behavior at room temperature [33, 37]. Recently, their ability to provide effective wear resistance at room and high temperatures has been explored. At 550 °C, electroless Ni–P coating with 10 wt.% P in as-deposited condition was observed to exhibit the best wear resistance [31]. The wear rate and COF dropped due the oxide glaze formation. As-plated Ni–P coatings show better wear resistance at operating temperatures near the phase transformation temperature [21]. Heat treatment was received by the coatings during the sliding wear at elevated temperatures. As a result, microstructural changes were induced and optimum grain size was achieved which prevented propagation of dislocation [21, 31]. The tough Ni matrix provides support to the oxide glazes and the tribological characteristics are enhanced. On the other hand, an aging effect takes place for the already heat-treated coating leading to deterioration in wear resistance and COF.

The high temperature tribology of Ni–P coatings with varying phosphorus content was investigated by Ghaderi et al. [12]. Wear behavior at high temperature for electroless nickel coating with 3.5, 5, 9, and 12 wt% phosphorous was studied. The range of changes in phosphorous content for Ni–P coating in between 3.5 and 12 wt% led to a change in hardness in the range of 555 and 710 HV. Wear resistance at high temperature for electroless coating was the highest and the lowest for Ni-3 wt% P and Ni-12 wt% P, respectively. Results show that in case of low phosphorous

electroless coating, an oxide film was formed, and this film led to the lubrication and a decrease in friction between the two surfaces subjected to wear while the worn surface of electroless high phosphorous nickel coating lacked an oxide film. The wear mechanism for these coatings was of adhesive type. When wear test ran over 750 m, electroless Ni–12 wt% P coating experienced adhesive and abrasive wear, hence they created more severe mass loss. Coating hardness after wear test at 250 °C for electroless Ni–9 wt% P increased by 10 Vickers. This happened because of grain growth and crystallization of nickel remaining from the amorphous phase. In case of low phosphorous coating, there was no hardness change.

High temperature tribology of electroless Ni–P–W coatings was investigated by Kundu et al. [22]. The influence of load, speed, and temperature on the tribo-performance as-plated and heat treated coatings was studied. Ni–P–W coatings exhibited a stable friction and wear behavior at 100–500 °C. The wear resistance of as-deposited coatings was particularly enhanced at 300–500 °C due to exposure at high temperature. An increase in microhardness of the as-deposited coatings post wear test substantiated the fact that the toughness of the coatings improved due to the heat treatment it received during sliding wear at elevated temperature. The predominant wear mechanism was adhesive as well as abrasive. The tribological performance of Ni–P-B coatings was governed by formation of MML, oxidative layer, and phase transformations [23]. Recent studies have revealed excellent tribology of electroless Ni–B deposits sliding against hardened steel at elevated temperature [42]. This is because of the high melting point of the hard boride phases. At high temperature of 500 °C, the worn surface of Ni–B coating was characterized by glazed oxide layer, depletion of boron, and oxidation [36]. At 300 °C (temperature near phase transformation), the wear rate observed for Ni–B coatings was lower than that at 500 °C (Fig. 7). Also as the temperature was increased to 500 °C, the COF decreased (Fig. 8) due to formation of low shear strength oxide layers. But the wear rate increased at 500 °C due to oxidation and depletion of B. It was further observed that high temperature stability of Ni–B coatings could be improved by deposition of ternary Ni–B–W and Ni–B–Mo coatings [34]. XRD of worn specimens at 500 °C revealed crystallization of the as-plated binary and ternary alloys. Inclusion of W improved the wear resistance whereas Mo improved the COF [34]. The tribological behavior of Ni–P–BN (h) coating deposited by electroless method was studied at 25–400 °C [27]. The COF and wear resistance both deteriorated with an increase in temperature. At 100 °C, failure of coatings took place by adhesive and fatigue mode. While at high temperatures, there was pronounced increase in adhesion due to softening of the coating and gross plastic deformation.

Franco et al. [11] observed an improvement in high temperature performance of Ni–P coatings at 200 °C on reinforcing SiC particles and heat treatment. XRD of worn track revealed phase evolution and slight crystallization at 200 °C. The worn surface of coatings without reinforcement indicated adhesive wear with micro-cracks. Sub-surface cracks were formed at high temperature due to the cyclic nature of loading during sliding wear. In Ni–P–SiC coatings, fine abrasive grooves and polishing were noticed. The reinforcement hindered micro-crack formation and a

Fig. 7 Wear rate of electroless deposited Ni–B coatings [36]. Reprinted from Tribology Transactions, 61, Mukhopadhyay et al., Effect of operating temperature on tribological behavior of as-plated Ni–B coating deposited by electroless method, 41–52, 2018, with permission from Taylor and Francis
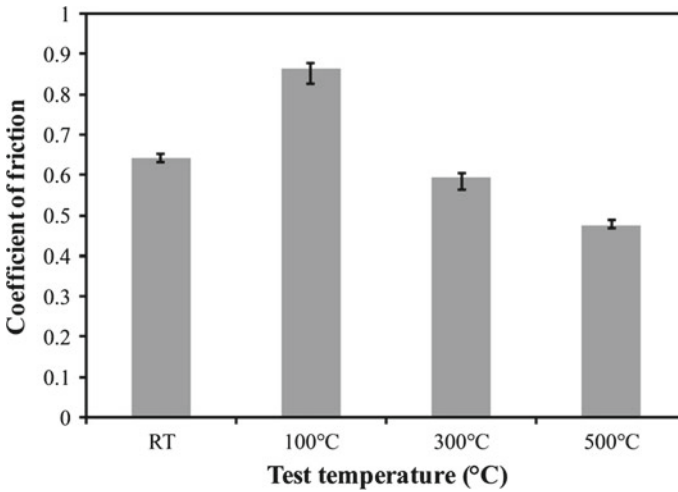
Fig. 8 Friction coefficient of electroless deposited Ni–B coatings [36]. Reprinted from Tribology Transactions, 61, Mukhopadhyay et al., Effect of operating temperature on tribological behavior of as-plated Ni–B coating deposited by electroless method, 41–52, 2018, with permission from Taylor and Francis

consequent reduction in wear rate took place. On inclusion of MoS_2 to form Ni–P–MoS_2 coating, the tribological behavior at high temperature improved due to formation of NiO and MoO_3 which have lubricating effects [28]. The COF decreased as the test temperature increased from 400 to 500 °C. But at 600 °C, the tribological characteristics deteriorated due to coating softening. Self-lubricating behavior at high temperature was also observed for Ni–P coatings with Ag and Ag + Al_2O_3 [1]. Silver particles decreased the fluctuations of friction coefficient and the coatings demonstrated a 'chameleon' behavior at elevated temperature.

3.5 Plasma-Sprayed and Plasma-Transferred Arc Coatings

A self-lubricating composite coating designated as PS304 was deposited on steam turbine governor valve lift rods. The high temperature wear and galling performance at 540 °C were investigated [58]. The chrome-oxide coating designated as PS304 was plasma sprayed. Silver and BaF_2/CaF_2 particles were co-deposited to function as solid lubricants. After 8500 h of operation, the surface of the rod was inspected. It was seen that the surface was well protected. The effective protection from wear and galling was due to formation of lubricious glaze. This protective layer consisted of barium/calcium fluorides, silver, and chrome-oxide.

Plasma spray technique was used to deposit nano-structured and ultra-fine WC–Co coatings [5]. The high temperature tribological behavior and failure mechanism were investigated. At high temperature, the nano-structured coatings had better wear resistance than ultra-fine coatings. In ultra-fine coatings, brittle fracture and adhesive wear were seen to dominate followed by abrasive wear. In nano-structured coatings, toughness fracture and abrasive wear were seen to dominate followed by adhesive wear.The wear rate and COF of TiC/Ti_3AlC_2–Co cermet coatings (deposited by atmospheric plasma spraying) at 600 °C were studied by [6]. Coated specimens with 30 wt. % Ti_3AlC_2 exhibited smallest COF and wear rate. Compared to TiC-Co cermet, the wear rate was 1.26 times lower. Whereas compared to TiC–Ni cermet, the wear rate of the coating was 10 times lower.

Plasma-transferred arc welding was used to deposit Colmonoy 5 powder on 316L stainless steel substrate [18]. The hardness of the coatings was 2.5 times higher than the substrate. As test temperature increased, wear loss and COF decreased. The wear track was characterized by severe abrasion and ploughing at room temperature during the initial sliding distance. The wear mechanism was shifted to delamination and mild abrasion as the sliding distance increased. For a shorter sliding distance at 573 K, the wear mechanism was mild ploughing. An increase in sliding distance shifted it to tribo-oxidation. Adhesive wear was observed at 823 K during initial sliding distance. Tribo-oxidation occurred at greater sliding distance. Plasma-transferred arc method was used to deposit hardfaced nickel based coatings [10]. The substrate material was gray cast iron. Even though hardness of gray cast iron was lower than the Ni coatings, both showed a similar wear rate due to formation of tribo-layer of C. Material softening occurred as a result of oxidation at 550 °C. Hence wear rate

increased abruptly for both the coatings and gray cast iron. The Ni based coatings were effectively protected by Ni–O. At 700 °C, the wear resistance of coatings improved. But the wear of gray cast iron was intensified. High amounts of oxide wear debris agglomerated to form an oxide layer which improved the wear resistance of the coatings.

3.6 Laser Clad Coatings

Laser cladding technique was used to deposit Ni60 and Ni60-hBN composite coatings on Ti6Al4V [29]. The coatings with 10% hBN exhibited excellent wear resistance at 300 and 600 °C. Wear performance of laser clad FeNiCoAlCu HEA coating was investigated at room temperature, 200, 400, 600, and 800 °C [17]. Oxide film formation resulted in excellent wear resistance of the coatings at high temperature. Abrasive and oxidative wear were dominant for the coatings at high temperature. CoCrNiSiBFe HEA powder was laser clad on low carbon steel and the wear behavior at high temperature was investigated [54]. At 500 °C, abrasive wear was observed for amorphous layer while whereas adhesive for the crystallized layer. This led to a decrease of 10% in mass loss of the amorphous layer.

4 Tribo-mechanisms Observed at Elevated Temperatures

4.1 Abrasive Wear

Abrasive wear may be characterized by the formation of parallel grooves along the direction of sliding. When the counterface material mates with the coated surface, due high hardness of the counterface, the asperities of the coatings may be sheared leading to the formation of wear debris. This may be useful or harmful to the elevated temperature tribological performance depending on the shape and size of the debris. The wear debris if small and spherical may cause a rolling effect thereby reducing friction and wear or it may cut through the coating creating grooves along the sliding direction and displacing material to the side of the wear track. A typical abrasive worn surface at 300 °C is illustrated in Fig. 9.

4.2 Adhesive Wear

Adhesive wear mechanism is observed when formation of bond between the two mating surfaces takes place due to high normal loads or high temperature. Bonding takes place due to adhesion and the contacts get sheared during sliding leading to the

Fig. 9 Abrasive wear
mechanism at elevated
temperature observed for
Ni–B coatings [35].
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tribological behavior of
electroless Ni–B coating at
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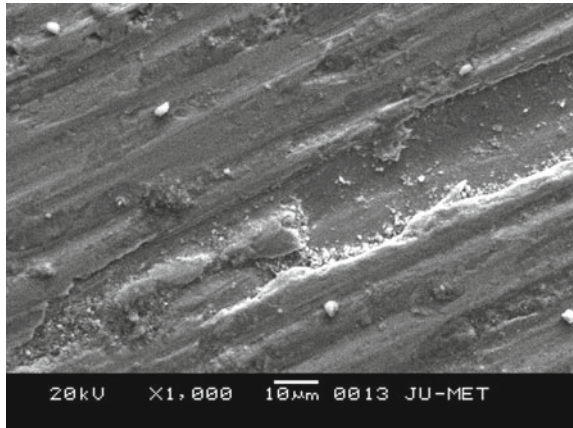
Fig. 10 Adhesive wear
mechanism at elevated
temperature for Ni–B
coating [35]. Reprinted from
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Effects of heat treatment on
tribological behavior of
electroless Ni–B coating at
elevated temperatures,
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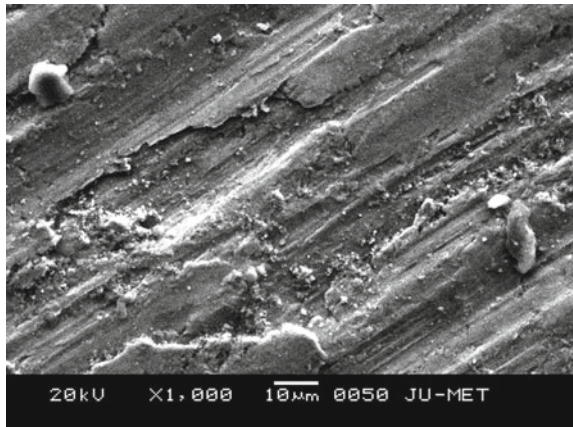
detachment of material fragments. Such surfaces are generally characterized by the
formation of 'pits' and 'prows' instead of parallel grooves or plastic deformation.
A surface with the formation of pit due to adhesion at high temperature (100 °C) is
shown in Fig. 10.

4.3 Fatigue Wear

At elevated temperatures, formation of cracks may take place during sliding wear
tests due to the repeated loading and unloading conditions prevailing. This leads
to the formation of crack. As due to the harsh conditions, accumulation of strain
becomes enough causing opening of the crack and its propagation. Due to repeated
cycles, surface or subsurface cracks are induced after a critical number of cycles,

Fig. 11 Fatigue-fractured surface of Ni–B coating at elevated temperature [35]. Reprinted from Surface Review and Letters, 24, Mukhopadhyay et al., Effects of heat treatment on tribological behavior of electroless Ni–B coating at elevated temperatures, 1850014, 2017, with permission from World Scientific Publishing Company
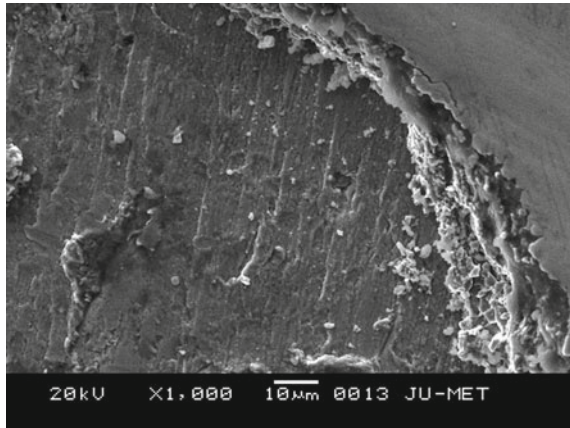
resulting in formation of large pits and detachment of materials. Wear caused due to fatigue wear is less crucial, but what is more important is the useful life in terms of number of cycles of operations before fatigue occurs. Material removal caused by fatigue wear and formation and propagation of cracks causing detachment of surface coatings at 500 °C is illustrated in Fig. 11. Micro-cracks are clearly visible in the SEM micrograph of wear track of electroless nickel coating (Fig. 11) during sliding wear tests at 500 °C.

4.4 Mechanically Mixed Layers (MML) Formation

MML formation is another important observation during wear tests at demanding condition. The tribology of a surface coating or a metallic material at demanding conditions is largely affected by this phenomenon. Wear debris is formed during the wear process due to adhesion, abrasion, fatigue, and a synergy of all these processes. This entrapped wear debris is flattened at different portions of the material as wear progresses. Moreover, some amount of the counterface material is also seen as transfer layers. This along with oxygen may form protective MML. These flattened areas act as load bearing sites and also leads to a smoothening effect causing a decrease in the specific wear rate or COF. MML formation and flattened areas as patches are depicted in Fig. 12.

4.5 Tribo-oxide Scales Formation

Formation of oxide layers which are protective in nature has been reported in several studies. This phenomenon is observed both under ambient as well as high temperature
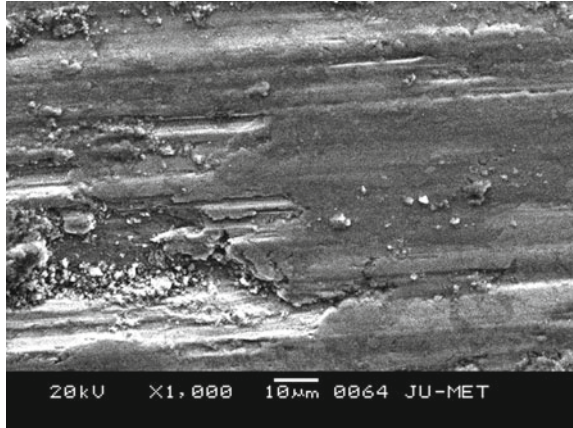
condition. A stable thick oxide layer formation results in improved tribo-performance of the metallic materials or coatings under demanding conditions as it tends to protect the layer below it. Though, periodic formation and removal of oxide layers may lead to unstable COF during the wear process and with high fluctuations in the same. When tribo-oxide patches are formed, reduction in specific wear rate is observed. The shear stresses caused during the sliding wear creates resistance to motion and act either within the tribo-patches or at the boundary between the patches and sub-surface material. Formation of blackish oxide layer at 500ºC sliding wear test for electroless nickel coating is illustrated in Fig. 13.
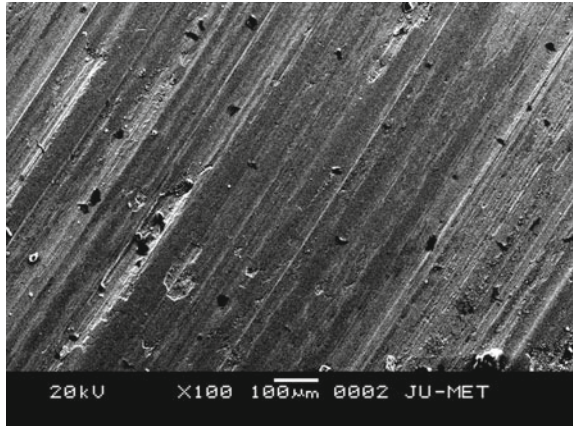
5   Conclusions and Future Research Directions

From the foregoing discussion, it can be seen that the investigation of tribological behavior of several materials as well as protective surface coating at high temperatures is gaining significant importance. With the rising demands of industries and aerospace applications, it is, therefore, necessary to obtain tailor made surface properties for components subjected to high temperatures. Among several methods discussed in this study, PVD-CVD coatings were seen to be largely explored for applications at high temperature. Even nickel coatings deposited by electroless method can be used as potential high temperature materials. This is because nickel has a high melting point. Furthermore, it is oxidation resistant up to 500 °C. The Ni–B variants also have high thermal stability. The use of reinforcements in metallic materials helps in dispersion strengthening of the matrix. A consequent improvement in wear and friction performance could be achieved. Various tribo-mechanisms are observed at elevated temperatures. These include adhesion, abrasion, fretting, fatigue, galling, MML, and oxide scales. A combination of the aforesaid wear mechanisms may be also observed. The synergistic effects of temperature as well as the wear mechanisms that occur determine the tribological behavior at demanding conditions. Therefore, the study of high temperature tribological behavior is necessary. Tailor-made coatings with nano-particles need to be explored further for providing effective protection at high temperatures. Nano-particle inclusion with self-lubricating ability and adaptability is the future of surface engineering for high temperature applications.

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