ABSTRACT: The present study focused on the development of NiMoAl-based self-lubricating composites using solid lubricants as the second phase by powder metallurgy. For this, Cr$_2$AlC MAX phase, Cr$_2$AlC–Ag, and MoS$_2$ powders were mixed with the NiMoAl-based matrix and subsequently hot pressed to produce bulk composite samples. The average hardness and wear resistance of the matrix were mixed with the NiMoAl-based matrix and subsequently hot pressed to produce bulk tribological properties, and some of their applications are in metallurgical components with the addition of solid lubricants. Solid lubricants are often preferred. In this regard, powder coking and volatilizing processes. To overcome these issues, the working temperature is increased slightly, because of the decrease in temperature and elevated temperature requirements, that is, there is hardly any single lubricant that meets both, low-temperature and high-temperature lubrication effects. Nickel–molybdenum (Ni–Mo)-based alloys have been introduced in the automotive sector to avoid scuffing-related problems. Ni–Mo alloys provide self-lubrication under dry conditions and also improve thermal conductivity. However, less run-in wear behavior and the abrasive nature are the main problems of Ni–Mo-based alloys. The performance of the Ni–Mo alloy was improved by the addition of aluminum (Al). The addition of Al strengthens the Ni–Mo alloy by the formation of tightly adherent alumina at high temperature that resists attack by oxidation, carburization, and chlorination. To further improve the wear resistance and high-temperature lubrication efficiency (to reduce CoF), additional solid phases, such as graphite, h-BN, MoS$_2$, and Ag, are used with the Ni-based matrix. NiMoAl has been described by micro Raman spectra.

1. INTRODUCTION

There is a potential demand for lubricating materials with low coefficient of friction (CoF) and reduced wear rate. However, most of the liquid lubricants lose their properties, if the temperature is increased slightly, because of the coking and volatilizing processes. To overcome these issues, solid lubricants are often preferred. In this regard, powder metallurgical components with the addition of solid lubricants were found to have huge potential because of their improved tribological properties, and some of their applications are in gas turbine seals, gears, transmission parts, brake bands, lining, and so forth. Conventional solid lubricants, such as molybdenum disulphide (MoS$_2$), graphite, inorganic fluorides, noble metals, and a few metal oxides possess lubricating effects under limited ambient conditions. MoS$_2$ is an attractive material because of its extremely low CoF and wear rate in the presence of other materials. However, the presence of humidity may decrease the performance of MoS$_2$. Graphite exhibits outstanding lubricating properties in a humid atmosphere. Hexagonal boron nitride (h-BN) has been an excellent solid lubricant for high-temperature applications because of its graphite-like lamellar structure. However, the poor sinterability and nonwettability of h-BN limit its applications. It appears that there is hardly any single lubricant that meets both, low-temperature and elevated temperature requirements, that is, having a low CoF and wear rate in a wide range of temperature. To overcome these issues, the use of composite lubricants has been suggested by many researchers. In the past years, nickel (Ni)-based metal matrix composites (Ni–TiC, Ni–Al–SiC, Ni–BN, and Ni–Cr–graphite) were reported to exhibit good tribological properties. Most of these composites are produced through the powder metallurgy route. Nickel–molybdenum (Ni–Mo)-based alloys have been introduced in the automotive sector to avoid scuffing-related problems. Ni–Mo alloys provide self-lubrication under dry conditions and also improve thermal conductivity. However, less run-in wear behavior and the abrasive nature are the main problems of Ni–Mo-based alloys. The performance of the Ni–Mo alloy was improved by the addition of aluminum (Al). The addition of Al strengthens the Ni–Mo alloy by the formation of tightly adherent alumina at high temperature that resists attack by oxidation, carburization, and chlorination. To further improve the wear resistance and high-temperature lubrication efficiency (to reduce CoF), additional solid phases, such as graphite, h-BN, MoS$_2$, and Ag, are used with the Ni-based matrix.
widely used in the automotive sector, and it exhibits a relatively high CoF of around 0.80 at room temperature. Slaney has reported that the addition of 10−20 wt % of a solid lubricant phase (graphite and MoS2) to the matrix (polyimide-bearing materials) improves the lubricating properties significantly without compromising its strength. Dangsheng reported that the addition of 20 wt % MoS2 in Ni−Cr (Ni−20Cr)-based alloys prepared by hot pressing shows the reduction in CoF from 0.46 to 0.21 at room temperature without compromising the hardness.

MAX phase materials have the general formula MXn+1AXn, where M represents a transition metal, A is a Group III or IV element of the periodic table, X is either C or N, and n ranges from 1 to 3. The MAX phase has properties of both metals and ceramics. The recent developments on MAX phase compounds such as Cr2AlC and Ta2AlC were reported to show good tribological properties. Their promising properties are attributed to the nanolaminated structure, with “MX” slabs with an interlayer of pure “A” element. The MAX phase materials have shown to possess remarkable tribological performance when tested against Ni-based superalloys at ambient temperature and 550 °C. Among all MAX phase materials, the Cr2AlC MAX phase possesses outstanding corrosion properties, which is useful for automotive applications. At ambient temperature, the existing literature demonstrated that the Cr2AlC MAX phase possesses a CoF of 0.65 ± 0.10. Further, the addition of silver to the Cr2AlC MAX phase (i.e., composites of Cr2AlC−Ag) was found to enhance the tribological properties significantly and reduce the CoF from 0.65 to 0.50 at room temperature.

It appears that the tribological properties of NiMoAl alloys, which are widely used in the automotive sector, may be enhanced further by using the Cr2AlC MAX phase and silver-added Cr2AlC MAX phase. Work function mapping using a scanning Kelvin probe (SKP) system is a convenient method to investigate the tribological properties of the materials. The application of SKP techniques in the field of tribology was in great demand over the years. Presently, it is the only technique that is sensitive to both surface and near-surface defects and allows the study of one of the two interacting surfaces during sliding. The Kelvin probe technique exhibits the highest sensitivity to the changes in the surface conditions. Zharin and Rigney made an extensive study of Kelvin probe techniques in tribological applications. The electron work function (EWF) from the SKP system is usually referred to the minimum energy required to remove an electron from the interior of a solid to a position just outside the solid. Studies of sliding of metal in contact, wear under ultralow loads, and investigation of changes during surface rubbing and changes in the contact potential of a hard disk drive in a humid environment are the few main areas of the SKP system for tribological studies. In the present work, attempts have been made to develop NiMoAl-based composites by the powder hot pressing method using Cr2AlC and Cr2AlC−Ag solid lubricants for improved tribological performance. The formation of the tribo film will be evidenced through the SKP system. Further, the known solid lubricant such as MoS2 powder has also been used with NiMoAl to carry out comparative studies on the tribological performance. The surface properties of NiMoAl−20 wt % Cr2AlC, NiMoAl−20 wt % Cr2AlC−Ag, and NiMoAl−20 wt % MoS2 were studied for the first time in the present work through SKP measurements. It has been observed that Cr2AlC addition to NiMoAl was more effective in improving wear resistance than MoS2 addition.

2. RESULTS AND DISCUSSIONS

Figure 1a−d shows the X-ray diffraction (XRD) patterns of NiMoAl-based hot pressed composites. The peaks correspond-
addition of a hard reinforcing phase to the matrix enhances the overall hardness of the composite. The MoS₂-based composite shows about 12% increase in the hardness compared to the base alloy (363 ± 10 HV). The addition of 20 wt % Cr₂AlC and Cr₂AlC–Ag to the NiMoAl matrix enhances the hardness by more than 75%. The hardness of pure phase MoS₂, Cr₂AlC, and Cr₂AlC–Ag are 4 GPa, 5.2 GPa, and ≈5–6 GPa, respectively.

The micrograph [back-scatter detector (BSE)] of the NiMoAl-based hot pressed composites has been shown in Figure 3a–d. In the base alloy (Figure 3a), there seems to be a phase separation where two distinct regions, that is, Mo-rich and Ni-rich, could be clearly seen. The Ni-rich phase (the gray region) is in the form of a continuous matrix on which the Mo-rich (the white region) discontinuous phase is dispersed along with the fine grains of Ni₃Al. Mo-rich grains are typically in the size range of 100–300 μm. No segregation of Al could be seen. When MoS₂ was added (Figure 3b), the composite seems to have a relatively fine microstructure compared to others. In this sample (MoS₂-added), Ni-rich (the gray region) seems to be in the form of a continuous matrix and Mo (the white region) of spherical shape and size in the range of 60–80 μm is distributed uniformly. MoS₂ is distributed near to the grain boundary and within the matrix. Zhang et al. reported that the addition of 10 wt % of MoS₂ to the NiMoAl matrix (80 wt % Ni–5 wt % Mo–5 wt % Al–10 wt % MoS₂) shows reduction in the hardness than the base alloy (90 wt % Ni–5 wt % Mo–5 wt % Al), and it was attributed to the segregation of MoS₂ near to the grain boundary, which further weakens the grain boundary sharply and reduces the strength. Cr₂AlC reinforcement has been found to change the microstructure significantly (Figure 3c). The grains of Mo (the white region), Ni (the gray region), and Cr₂AlC phase are clearly distinguishable. Grain sizes of Mo-rich and Ni-rich phases are relatively smaller as shown in Figure 3a. In the silver-added composite (Figure 3d), the grain around Cr₂AlC seems to be more fused, and the overall microstructure seems to be highly dense. Silver-rich or Ag₂Al regions were clearly seen, which are very fine in size.

Figure 4a shows the wear behavior of different samples as a function of sliding distance. The base alloy (NiMoAl) shows a continuous increase in wear loss with increasing distance. Wear loss has been reduced slightly by adding MoS₂ in the NiMoAl alloy. Upon the addition of the Cr₂AlC MAX phase, the wear resistance has further increased. The carbide phases in a metal alloy have been credited for excellent wear resistance because they act as protective barriers and resist the delamination of the surrounding matrix. The silver-added composite shows the best performance and very good wear resistance among all (Figure 4a). Compared to the NiMoAl alloy, the Cr₂AlC–Ag composite shows almost one-third reduction in wear loss. The trends observed during wear (Figure 4a) have also been reflected in the CoF (Figure 4b). Among all the samples, the NiMoAl alloy exhibits a very high CoF. The addition of 20 wt % of MoS₂, Cr₂AlC, and Cr₂AlC–Ag to the NiMoAl matrix exhibits significant reduction in the CoF by 52.18 ± 3, 55.43 ± 2, and 70.65 ± 4%, respectively. The CoF of MoS₂ (0.44)- and Cr₂AlC (0.41)-added composites are comparable. When the silver was added to the NiMoAl matrix, there is a considerable drop in the CoF as compared to the base alloys, and also, the curve was very smooth, compared to other composites (Figure 4b). Gupta et al. observed that the addition of silver (20 vol %) to the Cr₂AlC MAX phase exhibits a reduction in the CoF by 23%. However, in the presence of the NiMoAl matrix, the addition of 20 wt % of Cr₂AlC–Ag (preparation of Cr₂AlC–Ag is given in the Experimental Section) shows 34.15% reduction in CoF at room temperature as compared to 20 wt % of Cr₂AlC. The addition of solid lubricants to the NiMoAl matrix reduces the CoF and decreases the wear rate without compromising the hardness (Figure 2b).

Figure 5a–f shows the field emission scanning electron microscopy (FESEM) images, micro Raman spectra of the wear-tested samples, elemental analysis of the hot pressed (before wear testing) and wear-tested (after wear testing—samples surfaces. The NiMoAl sample shows surface deformations and large grooves; indicating the chipping-off of a large chunk of surface layers (Figure 5a). The formation of debris along with microcracks is observed on the worn surface. Chipping of the materials on the surface indicates the formation of a nonprotective tribofilm. Zhang et al. also observed the formation of shallow grooves and microcracks on the worn surface of hot pressed NiMoAl (90 wt % Ni–5 wt % Mo–5 wt % Al) sample. The elemental analysis displays that
all the prepared samples before wear testing is without any oxygen content (Figure 5f). However, after the wear testing, the samples contain the excess additional elements of oxygen (O), iron (Fe), and carbon (C). It is associated with the tribochemical reaction of the counter materials and the sample. Carbon and oxygen play an important role in the formation of a friction film, and it is related to the C–O adsorption layer.\(^{33}\) The tribolayer that is rich in carbon is also advantageous for the reduction in the wear.\(^{30}\) The micro Raman analysis shows the peaks corresponding to NiO and NiMoO\(_4\) (Figure 5e). The formation of NiO and NiMoO\(_4\) on the worn surface is associated with the oxidation of the NiMoAl sample by the tribochemical reaction on the rubbed surface during the friction process. The formation of NiMoO\(_4\) on the worn surface can provide lubrication for the sample as it is an effective high-temperature lubricant with low shearing strength.\(^{20,34}\) Deformation levels on the surface and grooves’ sizes have decreased significantly by the addition of MoS\(_2\) (Figure 5b). Deformation valleys are smaller and not continuous, unlike the NiMoAl alloy (Figure 5a). The distribution of in situ formed patchy oxide (NiO) was observed as an island on the worn surface along with the chipping of the material and the microcracks (Figure 5b). It appears that the formation of patchy NiO on the surface reduces the tribofilm integrity and causes spallation. An additional phase of MoO\(_2\) was also detected on the worn surface by micro Raman analysis (Figure 5e). The dioxide of molybdenum exhibits nearly similar lubrication performance as that of molybdenum disulfide\(^ {35} \) and thereby reduces the CoF and wear rate. The recent report\(^ {39} \) exhibits that the addition of MoS\(_2\) to the NiMoAl matrix does not play the expected lubricating role. It could be because of the fact that the MoS\(_2\) particles are agglomerated and do not form a continuous lubricating film. The appearance of chipping and microcracks on the MoS\(_2\) added composites in the present investigation is well in agreement with the reported study\(^ {29}\) (Figure 5b). The addition of Cr\(_7\)AlC has decreased these surface defects and the size of grooves (Figure 5c). The Cr\(_7\)AlC particles acting as a reinforcing phase are closely implanted on the worn surfaces, which effectively enhance the wear resistance of the sample. The surface has smaller grooves, which is distributed almost uniformly across the surface. The sample surface exhibits delamination behavior along with the abrasive wear. The micro Raman analysis shows the presence of Fe\(_2\)O\(_3\), NiO, NiMoO\(_4\), and Al\(_2\)O\(_3\) phases (Figure 5e). The formation of Fe\(_2\)O\(_3\) and NiMoO\(_4\) are providing adequate lubrication properties along with adhered Al\(_2\)O\(_3\) on the surface. Formation of Al\(_2\)O\(_3\) during the wear testing strengthens the tribofilm and improves the tribological properties. The possible tribochemical reaction of the Cr\(_7\)AlC grain is as follows

\[
\text{Cr}_7\text{AlC} + O_2 \rightarrow \text{Cr}_7\text{C}_3 + \text{Al}_2\text{O}_3 + (\text{CO or CO}_2) \tag{1}
\]

The worn surface of the Ag-based composite shows a relatively much smoother surface compared to all other samples (Figure 5d). Deformation and grooves have almost reduced, and the magnitude of surface defects is minimal because of the addition of silver. Silver with good self-lubrication properties can diffuse and accumulate on the rubbing surface to form a lubricating film and finally reduces the CoF. The uniformly distributed debris along with the adhered patchy oxide of Ag\(_2\)MoO\(_4\) was observed on the worn surface (Figure 5d). The surface wear scratches seem to be formed almost uniformly, indicating better wear resistance and tribological properties. Micro Raman spectra show a large number of mixed oxides, such as NiO, Ag\(_3\)MoO\(_4\), NiMoO\(_4\), and Al\(_2\)O\(_3\) (Figure 5e). It shows that the surface consists of a tribofilm containing a variety of oxides (Figure 5d). The possible tribochemical reactions have been given below\(^ {20}\)

\[
4\text{Ag} + 4\text{Mo} + 7O_2 \rightarrow 2\text{Ag}_2\text{Mo}_2O_7 \tag{2}
\]

\[
2\text{Ag} + 2\text{Ag}_2\text{Mo}_2O_7 + \frac{1}{2}O_2 \rightarrow 2\text{Ag}_2\text{MoO}_5 \tag{3}
\]

The formation of composite oxides including Ag–Mo–O and Al–O seems to be very advantageous, which reduces the wear as well as CoF.\(^ {36,37} \) The in situ formation or addition of soft phase in the matrix is advantageous because, during the repeated action of the applied load and the abrasive force, the softer phase will tend to wear out earlier. Further, these worn-out materials tend to fuse with the substrate under the mechanical force. As the wear process continues, the wearing out of the softer phase continues, which forms the tribofilm. This tribofilm, once extensive on the surface, plays a pivotal role in preventing further wear of the composite by reducing the direct contact between the two hard surfaces.\(^ {30}\)

The FESEM–energy-dispersive X-ray analysis (EDAX) elemental mapping of wear tested NiMoAl–20 wt % Cr\(_7\)AlC–Ag composite surface (as shown in Figure 6) shows the uniform distribution of silver oxides throughout the surface. Liu et al.\(^ {38} \) demonstrated that the addition of 20 wt % silver molybdate in NiMoAl (80Ni15Mo5Al) shows outstanding tribological properties at a wide temperature range. In the present study (NiMoAl–20 wt % Cr\(_7\)AlCAg), the

Figure 4. (a) Wear characteristics of different samples and (b) CoF characteristics of different samples.
in situ-formed Ag₂MoO₄ is the key factor for the reduction in the CoF.

The schematic mechanism of the SKP measurement and the work function difference plots are shown in Figure 7a–g. The
due to the formation of damaged surface film (NiO and NiMoO₄) (Figures 7b and 5e). During dry wear tests, the surfaces having higher differences in EWFs showed higher CoF. A similar behavior is observed in the reported study, which shows that when the surface film is damaged, the broken atomic bonds on the surface become active and lead to higher friction. Compared to the NiMoAl alloy, the MoS₂-added composite shows less surface damage and less Δϕ (Figure 7d), which is attributed to the formation of the MoO₂ lubricating conductive phase (Figures 7b and 5e). The Cr₂AlC MAX phase-added composites show a further reduction in the surface defects as compared to the above two samples. Even though the NiMoAl–20 wt % Cr₂AlC composite (Figure 7e) exhibits a slightly higher Δϕ as compared to the NiMoAl–20 wt % MoS₂ composite, it is associated with the formation of an adhered nonconductive Al₂O₃ phase, along with other oxides on the worn surface of NiMoAl–20 wt % Cr₂AlC (Figures 7b and 5e). The NiMoAl–20 wt % Cr₂AlCAg composite (Figure 7f) shows the least CoF (Figure 4b) and lowest EWF difference (Figure 7g), and it could be due to the formation of the highly conductive adhered Ag₂MoO₄ phase on the surface along with the Al₂O₃ phase (Figures 7b and 5e). The well-adhered tribofilm is protecting the surface from damage. The difference in the surface potential associated with the sliding leads to changes in the structure and the deformation influences the energy levels of the solid. Generally, for metals, the work function differences are reported because of the occurrence of plastic deformation. When conductive and soft metals such as silver and gold undergo significant plastic deformation, it leads to a decrease in the work function. As compared to the NiMoAl base alloy, the increases in the initial ϕ₁ (before wear testing) (Figure 7c–f) are related to the addition of different solid lubricant materials. However, after the wear testing, the changes in the ϕ₂ are dependent on the surface properties (conductivity of the tribofilm and the severity of surface defects), which stabilizes the friction regime. The obtained Δϕ in the present investigation depends on the conductivity of the tribofilm and the severity of surface defects, which is in agreement with the results reported by Zharin and Rigney.

Because the experimental conditions such as load, method of wear testing, and so forth, can affect the tribological behavior, the CoF of the NiMoAl-based composites obtained in this work is not directly comparable with the other existing literature. Possibly, there can be two effects on the field of tribology: (1) on a micron level, the damaged surfaces with oxide fragments tend to be rougher, which can reduce the overall contact area and hence imparting lower friction; (2) the friction can be further reduced because of the rotation of debris formed during the wear testing. The obtained results are significant to the material selection and the tribological aspects in the field of tribology. The MoS₂ and Cr₂AlC added composites shows enhancement in the tribological properties. In the presence of MoS₂ added NiMoAl composite, the surface exhibit the formation of spallation along with the segregation of patchy oxide (NiO), which reduces the integrity of the tribofilm. The Cr₂AlC added composite shows Fe₂O₃ pick up from the counter material, exhibits abrasion wear, and its CoF is comparable to the MoS₂ added composite. For automotive applications, the worn surface should possess the least possible surface delamination and abrasion wear. Among all the prepared NiMoAl-based composites, the NiMoAl–20 wt % Cr₂AlCAg composite exhibits least CoF, maximum reduced
wear rate, remarkable hardness, and least surface defects after the wear testing. The present study exhibits that the addition of the Cr$_2$AlC–Ag solid lubricant as the second phase is the most suitable for the enhancement of tribological properties of the NiMoAl matrix under ambient conditions for automotive applications.
3. CONCLUSIONS

This present work successfully modified the wear and tribological properties of NiMoAl-based materials by using Cr₂AlC and Cr₂AlC–Ag composite solid lubricants and compared this with MoS₂. The addition of 4 wt % silver (equivalent weight of silver in NiMoAl–20 wt % of the Cr₂AlC–Ag composite) to the NiMoAl matrix shows almost a one-third reduction in the wear loss and a considerable drop in the CoF of the NiMoAl matrix. The work function differences from the edge area to the grooved area clearly give an idea about the formation of the tribofilm in the grooved area, which is confirmed through SKP measurements. Among all the prepared samples, the NiMoAl–20 wt % Cr₂AlC–Ag composite exhibits excellent tribomechanical properties as compared to all the systems studied. A strong composite tribofilm of mixed oxides was found to provide good lubrication in the Cr₂AlC–Ag added sample. Based on the obtained results, it can be concluded that the NiMoAl–20 wt % Cr₂AlC–Ag composite is beneficial as a lubricating material with low CoF and reduced wear loss, especially for automotive applications.

4. EXPERIMENTAL SECTION

4.1. Preparation of NiMoAl-Based Composites. For the present work, nickel (Ni), molybdenum (Mo), and aluminum (Al) powders of about 50–65 μm and 99.2% purity were obtained from Powder Alloy Corporation (Loveland, USA). MoS₂ powder (99.2% purity, ~325 mesh) was obtained from Loba Chemie, and Ag powder (>99% pure, ~325 mesh) was procured from SRL India. This work synthesized various phases separately: (a) synthesis of the base alloy (NiMoAl), (b) synthesis of the Cr₂AlC MAX phase powder, (c) synthesis of the Cr₂AlC–Ag composite powder, and (d) synthesis of NiMoAl-based composites with different solid lubricants. Ni, Mo, and Al powders were mixed using a turbo mixer (room temperature, spin speed: 50 rpm, MXM 2, Insmart, and India-make) for about 2 h, in the weight percentage of 54, 44, and 2%, respectively. This mixed powder is henceforth designated as NiMoAl.

4.2. Preparation of Cr₂AlC MAX Phase and Cr₂AlC–Ag Powders. The Cr₂AlC MAX phase powder was prepared in-house, for the present study, using the method reported earlier with the same precursors and experimental apparatus. The resultant product was crushed and sieved using a ~325 mesh, to obtain the final Cr₂AlC MAX phase powder. Further, the Cr₂AlC powder was mixed with the 20 vol % Ag powder by using a turbo mixer for 3 h (room temperature, spin speed: 50 rpm, MXM 2, Insmart, and India-make). Then, the mixed powders were used to make pellets by a cold compaction press (~70 MPa). The pellets (Cr₂AlC–Ag) was sintered at about 1100 °C for 1 h under an argon atmosphere (flow rate 15 °C/min). The sintered sample was crushed and sieved (~325 mesh) to obtain the composite lubricant powder of Cr₂AlC–Ag.

4.3. Consolidation of NiMoAl-Based Composite Powders. In the next step, three different types of composite mixtures using 20 wt % of different solid lubricants were prepared by mixing for 2 h: (a) NiMoAl + Cr₂AlC, (b) NiMoAl + (Cr₂AlC–Ag), and (c) NiMoAl + MoS₂. Composite mixtures were consolidated by hot pressing (Vacuum Hot Press, VB Ceramics, India) using a graphite die and punch (15 mm dia.). The hot pressing was carried out at 1100 °C for 30 min of holding at a pressure of 50 MPa in a vacuum level of 10⁻³ mbar. To avoid sticking of the powders to the punch, boron nitride spray was used. The relative densities of the sintered samples were calculated by the geometric and Archimedes principles.

4.4. X-ray Diffraction Study. Phases on various samples were analyzed using an X-ray diffractometer (XRD, PANalytical, Netherlands, with a Cu Kα radiation of wavelength 1.54 Å).

4.5. Morphological Study. Surface morphology and composition of composites were analyzed by FESEM (FEI Quanta FEG 200), and EDAX (Flash Detector 610m: Bruker Nano GmbH), respectively.

4.6. Mechanical Characteristics. Microhardness (HV—Vickers scale of hardness) was determined by employing 0.3 N force (Matsuzawa, VMT-X) for 10 s. The tests were repeated ten times on the same sample, and the average values were reported.

4.7. Tribological Study. The wear behavior was investigated using a pin-on-disc tester with a wear & friction monitor (TR-20L-PH200—DUCOM, India) against a hard-counter material (hardened steel disc). The test parameters adopted were 2 kg load, a speed of 300 rpm, a sliding distance of 3350 m, and a track diameter of 60 mm. All the wear tests were performed at room temperature according to the ASTM G99 standard with a relative humidity of 55–60% under dry-sliding conditions, and an average of three measurements was reported. Worn surfaces were characterized using FESEM and EDAX. Micro Raman analysis (HORIBA France, LABRAM HR Evolution, wavelength: 633 nm, magnification: 50×) was performed on the worn surfaces to understand the oxide layer formation.

4.8. SKP System. To determine the tribofilm (in situ formed oxide), CPD measurements were carried out using a 2 mm diameter vibrational gold tip at a operating frequency of 78.3 Hz in the SKP system (SKP5050, KP Technology Ltd., UK). Work function differences (Δϕ = ϕ₁ – ϕ₂) from the edge area (ϕ₁) to the wear/groove area (ϕ₂) were analyzed. Then, between the conductive gold tip surface and the sample surface, the CPD was measured. An AC voltage, Vₐc(ω), with a vibrational frequency of 78.3 Hz was applied to the gold tip above the sample surface. Then, an electrostatic force, Fₑₙ, given by

\[ Fₑₙ = -\frac{∂C}{∂Z}(Vₑₚ - Vₛ)Vₛ \sin(ωt) \]

is sensed, when the gold tip comes near to the sample surface. The CPD was calculated by the surface potential (Vₛ) which is nullified by the outer voltage (Vₑₚ) through a feedback loop. As a consequence, the electrostatic force Fₑₙ between the sample surface and the gold tip was counterbalanced. The gold tip was calibrated through standard gold surface measurement for each NiMoAl composite’s measurement. All the experiments were carried out at ambient temperature. Further, the obtained CPD were converted to work function by using the following eq S as

\[ \text{work function} (ϕ) = 5100 - \text{CPD}_{ₚₐₜₜ} + \text{CPD}_{ₚₐₜₛₜ} \]

where 5100 is the actual work function of the gold tip in meV, CPDₚₚ is the CPD between the gold tip and the gold reference surface, and CPDₚₚ is the CPD between the NiMoAl composite surfaces and the gold tip. To have an average value of work function for the better interpretation, the Kelvin probe tip scanned the edge area to the wear area (groove) on the
surface of NiMoAl composites with an area of 19.36 mm² (raster scan), and the relative variation in the CPD was measured. The area of a single-pixel of SKP raster scan is 48 400 μm² (x step = 220 μm, y step = 220 μm, and total scan area = 19.36 mm²).

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