Fabrication and characterization of RF magnetron sputtered composite MoS_2 and ZrN coatings on Ti_3SiC_2 max phase for space applications

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Abstract. The lubrication effect of solid-based materials has been recognized for centuries, but their use as lubricants dates back to only about 50 years. Solid lubricants are used in applications where parts operate under severe operating conditions such as extreme temperatures and very high vacuum. Solid lubricants replace liquid based lubricants for operation under extreme environmental conditions that are beyond the capability of a liquid-based lubricant such as high or very high vacuum, high and cryogenic temperatures, radiation, corrosive gases, and fretting wear. Applications such as space mechanisms, satellites, space vehicles, turbopumps, nuclear reactors, refrigeration plants, etc are examples of such operating conditions.

In this research, nano scale composite coatings of $MoS_2$with varied proportions of ZrN (5%, 10% and 20%) were deposited on Ti_3SiC_2 Max phase substrate using Physical Vapour Deposition (PVD). The PVD technique used was the RF magnetron sputtering process. Material characterization was carried out using Field Emission Scanning Electron Microscope (FESEM) Spectroscopy and Energy Dispersive X-Ray Spectroscopy (EDS). Addition of ZrNis observed to reduce the porosity of the self-lubricating MoS_2 coating.

1 Introduction

Solid or solid based lubricating materials are thin films consisting of a single solid or composite material that are used to minimize friction and wear. To provide lubrication and minimize friction and wear, solid lubricants should have certain basic properties, i.e. low shear strength, good adherence to the substrate material, should have low abrasivity and also should be thermodynamically stable throughout the operating temperature range [1].

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Solid lubrication in bearings in space applications can be provided either by having a bearing component of the lubrication material itself (or a composite material) or by coating it with a solid lubricant so that there is no need for external lubrication [2].

Lamellar solids demonstrate low coefficient of friction (CoF) due to low shear strength in specific directions. Soft metals with high plasticity, such as lead, tin, bismuth, and silver, have lubrication characteristics and can be applied as thin films on substrates to reduce the CoFdrastically.The lubrication effect of metal oxides such as PbO and MoO_3can be seen at higher temperatures due to increased ductility that substantially reduce the coefficient of friction [3].

Organic materials such as PTFE are also used in some applications for lubricating purposes. PTFE is an organic polymer with a chain structure and its molecules readily shear due to poor bonding with the surrounding molecules and thus have a low coefficient of friction. However, it cannot be used for high load applications as it is relatively soft and has low resistance to wear. This can be enhanced with the use of suitable filling materials such as graphite, MoS_2, and glass fiber [4].

Graphite is an allotropic form of carbon. Similar to hexagonal boron nitride and MoS_2, it has a layered structure having covalently bonded carbon atoms in the plane and a weak van der Walls bonding within the layers. It has a hexagonal crystalline structure with a bond length of 0.14 nm and a width of 0.34 nm between the planes as shown in Figure 1.1. A single graphite layer is called graphene. The lubrication effect in graphite is due to the intercrystalline slip between two planes. It has a glossy black look and it feels smooth and sleek to the touch. Graphite carbon atoms are bound to only three neighboring atoms rather than to four with one electron free to pass in the plane, making graphite electrically conductive [5]. The lubrication properties of graphite are strongly affected by atmospheric conditions. It provides better lubrication in a humid atmosphere than in dry atmospheric conditions [6].

Sputtering is one of the most popular and extensively used coating deposition processes, falling under the category of PVD. The deposition process takes place in an evacuated chamber that has been pumped down to a very low pressure (about 10^{-7} mbar). It involves using highly charged ions to expel atoms from a target material onto the surface of a substrate. Plasma is created by ionizing an inert gas such as Argon, where the Ar+ ions are propelled towards the cathode target material by assigning a high voltageto the target. The highly energized gas ions hit the target material and overcome the binding energy of some of the atoms on its surface and dislodge them. These ejected atoms are deposited on the substrate surface leading to the nucleation of a thin coating. DC, Pulsed DC, RF or HIPIMS power sources are used to generate a plasma in the sputtering process [7]. Compared to other PVD methods, the key benefits of sputtered MoS_2 coatings include improved adherence to the underlying substrate, increased density, and higher purity, This results in reduced CoFand increased wear resistance of the coated parts[8].

Curry *et al.,* examined the impact of MoS_2 microstructure on tribological results. MoS_2 with two different microstructures were deposited on two different stainless steel substrates. A highly oriented MoS_2 film having basal (0001) planes parallel to the substrate was deposited on 17-4 PH steel using the N_2 spray technique, and an amorphous MoS_2 film on AISI 440C was deposited using the DC magneteron sputtering technique. XPS, MD, high sensitivity low-energy ion scattering (HS-LEIS), and tribological tests showed that highly oriented (0001) MoS_2 films are more resistant to oxidation and need a much shorter run-in time to achieve a steady state friction coefficient than amorphous films, which need much longer run-in cycles. However it was observed that at higher temperatures degradation of coatings due to increased oxidation was detrimental to the coating behaviour[9].

Spalvins investigated the effect of deposition parameters on the structure and tribological performance of sputtered MoS_2 coatings. In the study, the coatings were applied on AISI 304 stainless steel substrates. The substrate temperature and voltage bias proved to have a critical role in the development of coating structure and the resulting tribological properties.The coating structure changed from amorphous to crystalline when the substrate temperature increased from -195°C to 320°C, with a grain size of 10 Å at -195°C, 50 Å at 20°C, and 100 Å at 320°C. The coefficient of friction decreased by an order of magnitude as the structure changed from amorphous to crystalline. It was also reported that subsrate biasing after -150 V DC resulted in increased friction and that no lubrication properties were observed after -350 V DC biasing [10].

Stupp investigated the consequence of metal doping on tribological characteristics and endurance of sputtered MoS_2 coatings. In this research, various metal dopants such as Cr, Mo, Ni, Cr, etc were investigated. Metal doped MoS_2 coatings were found to have improved lubrication properties and better endurance than undoped coatings. However, increasing metal concentration beyond a certain limit was found to adversely affect the lubrication performance of these coatings. In fact, a metal concentration of 5-8% has been proposed as optimal for sliding contacts [11].

Wahl *et al.,* studied the frictional behavior and endurance of Pb-Mo-S coatings. The coatings were deposited on distinct steel substrates using an ion-beam-assisted deposition technique. Sliding friction tests were carried out against 52100 steel balls on a ball-on-disc tribometer. Coating characterization was done using RBS, XRD, Raman spectroscopy and scanning Auger microscopy. The composite coating demonstrated improved tribological performance due to higher density, better adherence, low shear strength, lower coefficient of friction and higher shear strength[12].

Zabinski *et al.,* studied the outcome of doping on the tribological properties of MoS_2 coatings. Morphological observations of Ni, Sb_2O_3, Fe, and Au dopants showed that they improve film density, hardness, and cystallite size. Sb_2O_3 doped coatings were observed to have improved hardness, density, and a very fine microstructure. The COF of MoS_2/Sb_2O_3/Au coating has been found to be 0.06 in air and 0.02 in dry N_2.The optimal doping concentration for lowest COF was 35 weight percent for Sb_2O_3[13].

Su and Kao studied the structural, mechanical and tribological evolution of MoS_2 coatings with varying concentrations of Cr doping. The depositions were carried out on M2 steel substrates using the closed field unbalanced magneteron sputtering process with a Cr adhesion layer and an intermediate CrC layer. The varying percentage of Cr was obtained by varying the Cr target current during the deposition process. It was found that with an increase in Cr content, the coating hardness also increases and the coating becomes more amorphous. Moreover, the test scratch test results revealed that 5-15%-Cr improved the coating adhesion. However, increasing Cr content beyond 8% affected the tribological performance, therefore 5-8%-Cr concentration was found to be optimum for good adhesion and improved friction and wear behaviour [14].

Banday and Wani studied the mechanical properties and wear behaviour of Ti/MoS_2/Si/MoS_2 multilayer coating. A nanoscale coating of 170 nm thickness was fabricated on Al-Si substrate using PLD. Nanoindentation and nanoscratch tests were performed against a Berkovich diamond indenter to determine mechanical properties. A maximum hardness of 33.93 GPa corresponding to a load of 2000 µN was obtained with an excellent adhesion upto 5000 µN. Furthermore, the CoF and specific wear rate of the coating were observed to be as low as 0.09 and 3.3×10^{-10} mm^3/Nm, respectively [15].

Zabinski *et al.,*carried out the tribological and compositional characterization of PbO-MoS_2 composite coatings. The coatings were deposited on 440C steel substartes using the PLD technique with different PbO: MoS_2 composition targets.The coatings from each target were deposited at 300 K and 573 K followed by different levels of post process annealing. The coatings deposited at 300 K were amorphous as they showed featureless Raman spectra. However, after annealing at 773 K in air or tribo-mechanical stressing, the films produce crystalline MoS_2, $PbMoO_4$ and MoO_3. Because $PbMoO_4$ and MoO_3 are lubricious at higher temperatures, and MoS_2 provides lubrication at low temperatures, these coatings have the properties of temperature adaptive chamaleon coatings.Moreover, all the coatings exhibited better friction and wear performance than PbO or MoS_2 during tribotesting [16].

Teer *et al.,* developed a MoS_2/Ti composite coating and examined its friction, wear and adhesion properties. The coating was fabricated on M42 steel using the CFUBMS process and has a multilayer pattern with alternate layers of MoS_2 (10 nm) and Ti (< 1 nm). The coating demonstrated remarkable tribological properties and was registered under the trademark MoST. It showed a friction coefficient of 0.02 and could survive more than 10,000 cycles at 100 N at 40% RH. Moreover, in the progressive load scratch test, the coating demonstrated good adhesion up to 120 N [17]. Further investigation of MoST by Fox *et al.* found that the coating has an amorphous structure and also no multilayer structure, but Ti is present as a solid solution in MoS_2. Nanoindentation results showed that MoS/Ti has excellent mechanical properties having hardness more than 15 GPa and Youngs modulus of 238 GPa [18].

Ye *et al.,* investigated the effect of Zr concentration on tribological and microstructural properties of MoS_2-Zr composite coatings. The coatings were deposited using CFUBMS and the Zr concentration was controlled by varying the target current. The microstructural studies revealed that as the Zr content increases (0 – 9.76%), the coatings get denser and the MoS_2 crsytalline peaks gradually disappear. MoS_2-Zr coatings have higher hardness (H = 9.8 GPa) and Young’s modulus (E =132 GPa) values than pure MoS_2 (H= 7.1 GPa and E = 88 GPa, respectively). The critical scratch load for all Zr doped coatings was more than 60 N as compared to 10 N for pure MoS_2. The coating comprising 9.76% Zr has a low COF of 0.04 at 20 N load at 68% RH [19].

The addition of metals (Cr, Pb, Ag,Ti, W, Ce, Au,Nb, Ni) to MoS_2 coatings in ambient air is one of the most successful and cost-efficient strategies to increase mechanical and tribological characterization. As a result of its low COF and high hardness in humidity, MoS_2 with metal is gaining popularity [20-25]. So far there has been no study employing sputtering for deposition of MoS_2 with 5%, 10%, or 20% ZrN coatings on Ti_3SiC_2 substrate yet, as evidenced by the literature.

2 Materials and methods

The Max PhaseTi_3SiC_2samples were polished using an Auto Polishing Machine (BANIMOUNT-P Auto Chennai, India) to get the desired surface finish as shown in Figure 1. The samples were initially ground using abrasive embedded papers of 220 grit, 600 grit and 1200 grit for 10 min each. Polishing was finallycarried out using velvet cloth and diamond paste with abrasive grit of 3 µm, 1 µm and 0.25 µmfor 3 minutes each. Surface roughness (Ra) of around 25 nm was achieved for all processed samples of Ti_3SiC_2. MoS_2 and MoS_2/ZrN composite coatings (1µm thickness) were deposited on Ti_3SiC_2substrate with varying percentages of 5%, 10% and 20% ZrN to improve the friction and wear properties. The influence of ZrN addition with MoS_2 coating on the hardness, adhesion strength and nanotribological properties is studied. Table 1 shows the parameters used to develop the various coatings using the RF Magnetron Sputtering process.

Table 1. Deposition parameters

Temperature	**RT**			
Pressure (mbar)	7x10^{-3}			
MoS_2 target power (W)	65 (RF)			
ZrN target power (W)	0	30	45	65
	0%	5 %	10%	20%
Coating thickness	1 µm			

Characterization of deposited coatings involves determining the film thickness, chemical composition, crystallographic structure, and surface morphology.

Thecoatings of MoS_2 and MoS_2 with additions of 5%, 10%, and 20% ZrN were measured utilizing an optical 3D profilometer (Rtec. the USA). FESEM was used to examine the surface topography of the coated samples.

The topographical and 3D surface images, surface roughness, coating thickness and depths of wear scars were determined using an Rtec 3D optical profilometer with AFM and optical microscope (Leica DM6000 M). The combination of different optical techniques on the same system in 3D profilometer allows for the precise measurement of surfaces with nm resolution. The surface topography and the 3D surface images of the polished samples and the coatings were produced by scanning the surfaces. Furthermore, the surface roughness, R_a, of the polished samples and coatings was calculated using Gwyddion and Hystriontriboview software.

The coating thickness was determined using a masking technique. During the coating deposition, the sample was masked with an adhesive tape and after the deposition was completed, the tape was removed and the difference in the height of the coated and the uncoated surface was measured at five different positions using the optical profilometer and the coating thickness was taken as an average of these measurements.

The field emission scanning electron microscope (FESEM) is a very powerful tool for determining surface morphology and structure of materials. Compared to a conventional SEM, FESEM has a much brighter source of electrons and a smaller size of electron beam than a conventional SEM, allowing for observation and imaging magnifications of up to 500K x. FESEM also has the benefit of being able to produce high resolution images with very low accelerating voltages. This improves the ability to observe ultrafine surface properties, materials sensitive to electron beams, and non-conductive materials. FESEM images of the substrate material (AMS 5898) and the coating was obtained using ZEISS GeminiSEM 500 at CRFC Lab, NIT Srinagar. During the whole process the system vacuum was maintained below 1×10^{-5} mbar.

3 Results and discussions

Fig. 1 (a, b) shows the 3D surface profile and average surface roughness of the Ti_3SiC_2 substrate. A surface finish of 27 nm was obtained for all samples after polishing. The sputter coating process was used for deposition of MoS_2 and MoS_2 with 5%, 10%, and 20% ZrN coatings on Ti_3SiC_2 substrates. For coating purposes, targets of MoS_2 (purity 99.9%) and ZrN (purity 99.9%) of 50.8 x 6.35 mm were used on a Ti_3SiC_2 substrate. A uniform coatings thickness of 1 µm was obtained after several trials.

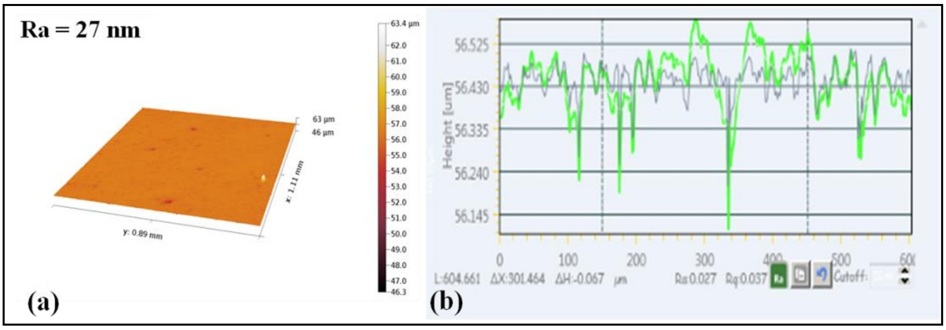

Fig. 1. (a) 3D surface profile (b) average surface roughness of Ti_3SiC_2 Max Phase substrate

FESEM morphology of the coated sample surfaces is shown in Fig. 2 (a-d). The imaging displays that the grain patterns are homogenously spread over the substrate's surface. Fig. 2 (a-d) further shows that when ZrN is added to the MoS_2, the grains became finer than the MoS_2 coating without the addition of ZrN. Fig. 3 (a-d) shows the EDS of MoS_2 coating and MoS_2 coating with additions of 5%, 10%, and 20% ZrN. Presence of Mo, S, Zr, and N can be observed in Fig. 3 (a-d), indicating that the intended MoS_2 and MoS_2 composite coatings have been successfully deposited on the respective substrates.

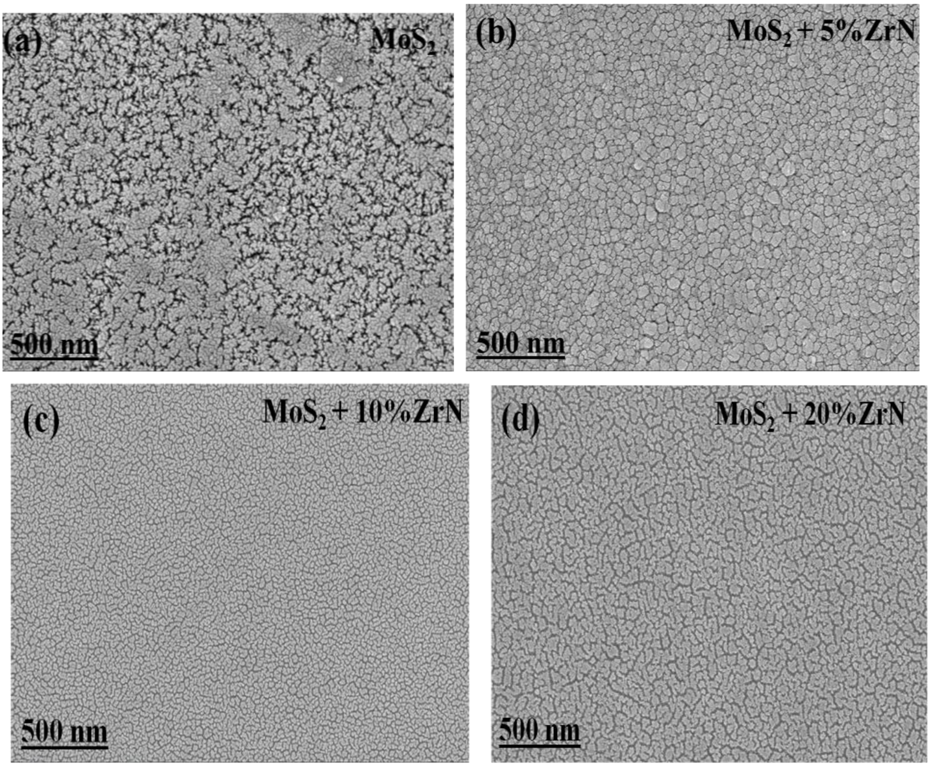

Fig. 2. FESEM images (a) MoS_2 coating; (b) MoS_2 + 5% ZrN; (c)MoS_2 + 10% ZrN
(d) MoS_2 + 20% ZrN

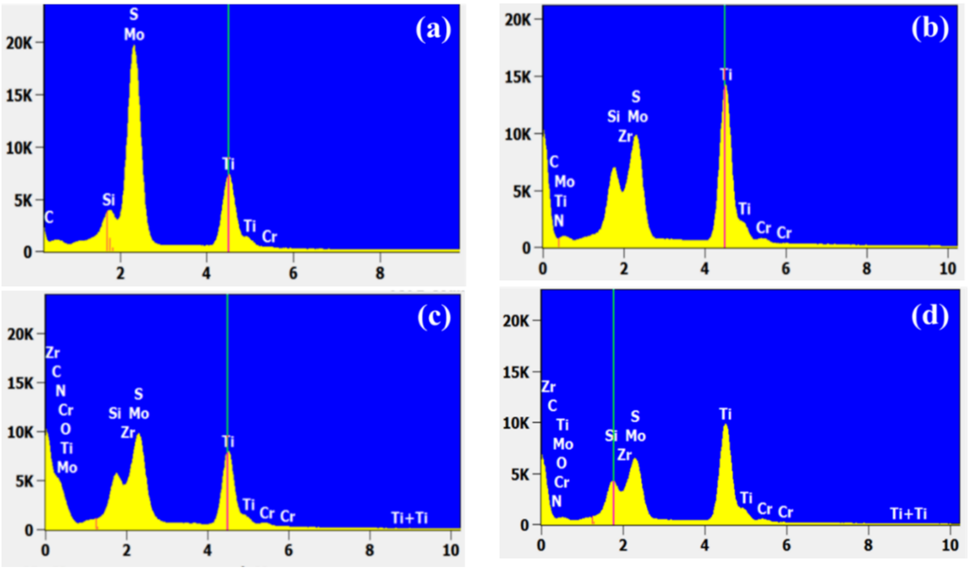

Fig. 3. EDS of (a) MoS_2 coating; (b) MoS_2 + 5% ZrN (c); MoS_2 + 10% ZrN; (d) MoS_2 + 20% ZrN

4 Conclusions

The addition of ZrN in MoS2 increases the densification of the otherwise porous pure sputtered MoS2 coating as observed in the FESEM imaging of the respective 0%, 5%, 10% and 20% ZrN coatings. The technique of RF magnetron sputtering is especially effective in developing uniform and homogenous composite coatings of desired compositions for use in extreme environments of near and outer space. The physical and tribological properties of the developed composite coatings have to be evaluated further to determine the ideal composition of ZrN to achieve optimum wear resistance and simultaneously lower CoF.

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