Adhesion Property of Self-lubricating Si/MoS2 Nanocoating at Nano-scale Level

Sumaira Banday, M.F.Wani*, M.Junaid Mir, Bisma Parveez
Tribology Laboratory, Department of Mechanical Engineering, National Institute of Technology, Hazratbal, Srinagar, J&K, India-190006
E-mail: *sumaira_03phd13@nitsri.net

Abstract. Nanoscratch test was performed on self-lubricating Si/MoS2 nanocoating of 115 nm thickness prepared by pulse laser deposited technique on Al-13Si substrate. The surface morphology and surface elemental analysis of Si/MoS2 nanocoated sample were studied using Scanning electron microscope integrated with Energy dispersive X-ray spectroscopy. The structural analysis of Si/MoS2 nanocoating was conducted using X-ray diffraction and Raman spectroscopy. Nanoscratch tests were conducted at low load of 250-1250 µN to examine the adhesion, deformation and failure behaviour of the coating/substrate system. The results indicate that Si/MoS2 nanocoating show better adhesion strength at low loads. Also, in-situ scanning probe microscope images of Si/MoS2 nanocoating shows plastic flow of coating with no debris and cracks on the surface. Therefore, the wear mechanism is mostly ductile and abrasive.

1. Introduction
The tribological behaviour of mostly used transition metal dichalcogenides (TMD) i.e., WS2 and MoS2 coatings have been studied by various researchers [1-3]. Among various TMD, MoS2 is most widely used because of its layered structure. MoS2 has sandwich type molecular structure in which molybdenum (Mo) layer is sandwiched between sulphur (S) layers. The bond between S-Mo-S is bonded by strong covalent bond due to which it has the ability to sustain high load, Whereas S-Mo-S layers are bonded by weak van der Walls force, which attributed lubricating property of MoS2 [4].

MoS2 coatings exhibit lubricating properties in water vapour-free and in ultrahigh vacuum environment. In humid air, unsaturated or dangling bonds on the edge of basal planes reacts with the moisture and oxygen in environment, resulting in higher friction and coating failure. However, there is an increasing demand for developing environmentally friendly solid lubricant coatings that can adopt themselves to different environments [5]. Donnet et al. [6] analysed the friction of MoS2 coating in ultrahigh vacuum, high vacuum, dry nitrogen and ambient air, the coefficient of friction (COF) increases in the same order. Fusaro [7] investigates the tribological properties of MoS2 coating in dry air, moist air and dry argon and observed that wear rate and COF were highest in moist air, suggested that the water causes reduction of MoS2 lubricity. Recently, addition of metal or ceramic elements to MoS2 coatings improves the lubricating and corrosion phenomenon of coating [8-10]. It was found that the addition of metals (Ti, Pb, Cr, Nb, Ce, Au, Ni) and ceramics (TiN or TiB2) [8, 11-15] improves the hardness and wear resistance of the MoS2 coating in different environments.

Several thin films deposition techniques have been applied for coatings. Researchers have studied the tribological and mechanical properties of coatings deposited by various techniques, such as, PVD, PACVD, magnetron sputtering, thermal spraying, ion implantation, fluidized bed, and pulsed laser deposition (PLD) [16-22]. Among various Physical vapor deposition processes, PLD is simplest, environment friendly and convenient process for coatings [23]. In PLD technique, the material to be deposited is vaporized from the targets by focusing laser radiation and the desired substrate is deposited with ablated vapour [24]. Laser conditions used determine the evaporation process of
material from target can be either non-thermal or thermal. In addition, PLD has a potential for stoichiometric transfer of the material from target to the substrate. Thus PLD is effective for deposition of complex oxide and chemically inert films with exact stoichiometry [23,25]. It is evident from the above literature review that coatings can be developed by various surface coating methods, like PVD, PACVD, magnetron sputtering, thermal spraying, ion implantation, fluidized bed, and pulsed laser deposition (PLD) [16-22]. Moreover, the mechanical and tribological properties of MoS2 coating in moist environment can be improved by addition of ceramics and metals [8,11-15].

Light weight materials such as Al alloys are used for manufacturing various components; viz, bearing, cylinder liners, piston and piston rings connecting rods etc. Light weight material helps in increasing efficiency, reducing fuel consumption and preservation of the environment. Bearings are used in various assemblies in automobile and aerospace industries. The endeavour of designers and engineers is to replace conventional materials with light weight materials of bearings. Light weight materials used for the bearing is aluminium alloys; Viz, 2xxx, 4xxx and 7xxx series. The Al-Si alloy is mostly used for bearing application because of its excellent bearing qualities and good compressive strength. Researchers have also observed that Al-Si alloys shows higher wear rates which can be reduced by applying surface coatings.

However, the deposition of Si/MoS2 nanocoating on Al-13Si substrate by PLD or by any other surface coating technique has not been reported in literature till now.

Researchers have studied tribological properties of Si-DLC coating and observed that Si content reduced the wear and the friction coefficient of the mated component, although the wear of the coating increases with increase in Si content. Silicon particles at the bearing surface function as a polishing agent that moderates shaft surface roughness and adapts to maintain oil film integrity. The aim of this research work is to deposit self-lubricating nanocoating of Si/MoS2 on Al-13Si substrate as a backup lubricant for situation where the liquid lubricant fails or is incapable to prevent metal-to-metal contact in case of Al alloy bearing. Nanoscratch tests were conducted at low load of 250-1250 µN to analyse the adhesion deformation and failure behaviours of the coating/substrate system.

2. Experimental methods

Pulse Laser deposition conditions

Before deposition of coating the Al-13Si substrate was polished to nano-scale level. Silicon-carbide abrasive papers of various grit size and diamond paste with different particle sizes were used to obtain the final surface roughness in nanometers. High purity targets of 99.9% MoS2 and 99.9% Si were used for deposition of Si/MoS2 nanocoating with a pulsed Nd: YAG laser system operating at 355 nm wavelength, 2.5 Joules pulse energy and 6 ns pulse duration with a repetition rate of 10 Hz.

2.2 PLD coating design

Thin surface coating deposition of Si/MoS2 on Al-13Si substrate was carried out in 2 steps. In first step, a thin film of Si was deposited for 30 minutes on Al-13Si substrate, which was followed by depositing MoS2 for another 30 minutes on the Si layer. The final thickness of Si/MoS2 coating is 115 nm.

2.3. Coating surface morphology and testing

Surface morphology and surface elemental analysis of Si/MoS2 coated samples was carried out by Scanning electron microscope (SEM) and Energy dispersive X-ray spectroscopy (EDS), respectively. X-ray diffraction (XRD) and Raman spectroscopy were used to study the structure of Si/MoS2 nanocoating deposited on Al-13Si substrate. Si/MoS2 nanocoating thickness of 115 nm was measured using ellipsometry. SEM, EDS, XRD and Raman spectroscopy of Si/MoS2 coating is reported somewhere else.

Low constant load 250 – 1250 µN nanoscratch tests on Si/MoS2 coated samples with a scratch length of 10 µm were conducted at a room temperature to investigate the adhesion and wear mechanism.
3. Results and discussion

Si/MoS2 nanocoating characterization

Surface morphological studies and surface elemental analysis of Si/MoS2 nanocoating shows a random distribution of grains on the Al-13Si substrate and the contents of Mo, Si, S, and O, elements on the surface at three different points. Also, Oxygen content was detected in the EDS spectrum which indicates presence of porosity in the coating. SEM and EDS of Si/MoS2 nanocoating is reported somewhere else. Figure 1(a-b) shows the high magnification cross-sectional and top images of the coated sample and it is clear from Figure 1(a-b) that coating has been deposited on the Al-13Si substrate.

![Figure 1](a) Cross-section image of Si/MoS2 coating (b) Top 3D image of Si/MoS2 coating using scanning probe microscope

XRD pattern of Si/MoS2 coated samples shows the typical diffraction peaks correspond to MoS2 phases are (0 0 2), (1 0 0) and (1 1 0). Similar results were obtained by the research for MoS2 coating [26]. Raman spectra were obtained using laser power of 50 mW and 60 second exposure time. The study of surface coatings, using Raman spectroscopy clearly shows the peaks lying between 200 cm⁻¹ and 500 cm⁻¹ that is the evidence of the presence of MoS2. XRD and Raman spectroscopy of Si/MoS2 nanocoating is reported somewhere else.

Nanoscratchwear behaviour of Si/MoS2 nanocoating

Table 1 shows the nanoscratch property of Si/MoS2 coating. It is clear from Table 1 that the scratch depth is 10.37 nm at maximum load of 1250 µN, which is less than the coating thickness of 115 nm. Thus, the diamond tip is scratching within the coating, which attributes strong adhesion of Si/MoS2 coating with Al-13Si substrate. Figure 2 shows the scratch depth Vs constant normal load. Constant normal load nanoscratch experiments were carried out to analyse the rates of sliding/abrasive wear. From Figure 2, it is clear that scratch depth increases with increasing load as the contact area increases with increasing constant normal load.

| S. No. | Load (µN) | Type of Loading            | Scratch Length (µm) | Scratch Depth (nm) | COF |
|--------|-----------|----------------------------|---------------------|--------------------|-----|
| 31.    | 250       | Constant Load Scratch      | 10                  | 2.18               | 0.13|
| 2.     | 500       | Constant Load Scratch      | 10                  | 4.92               | 0.13|
| 3.     | 750       | Constant Load Scratch      | 10                  | 7.79               | 0.14|
| 4.     | 1000      | Constant Load Scratch      | 10                  | 9.61               | 0.14|
| 5.     | 1250      | Constant Load Scratch      | 10                  | 10.37              | 0.15|
Figure 2. The dependence of scratch depth of Si/MoS$_2$ coating on load.

The 2D and 3D scratch marks on Si/MoS$_2$ coated sample are shown in Figure 3. It is clear from SPM images that Si/MoS$_2$ coating scratches displays smooth scratch track with no debris and cracks on the surface. Furthermore, coating material is piled up and remains intact to the surface, which indicates that the plastic deformation occurred during scratching. Thus, the wear mechanism at room temperature is mainly ductile and abrasive which results in constant and low COF as shown in Figure 4. Also, COF decreased slightly with increase in scratch length, which indicates that the Si/MoS$_2$ nanocoating has a remarkable lubricating effect. It is also observed that COF remains almost constant with the increase in load because with the increase in load the indenter tip remains within the MoS$_2$ coating, which is deposited on the top of the Si layer and results in almost constant COF.
Figure 3. The SPM 2D and 3D Scratch images of Si/MoS$_2$ coated sample at 250 µN (a,b) 500 µN (c,d) 750 µN (e,f) 1000 µN (g,h) 1250 µN (i,j).

Figure 4. The dependence of COF of Si/MoS$_2$ nanocoating with time.
4. Conclusion
In this research work, adhesion property of the Si/MoS\textsubscript{2} nanocoating on Al-13Si substrate was carried out. Si/MoS\textsubscript{2} nanocoating shows better adhesion strength with Al-Si substrate at low loads. In-situ scanning probe microscope images of Si/MoS\textsubscript{2} nanocoating shows plastic flow of coating with no debris and cracks on the surface and the wear mechanism is ductile and abrasive. Also, COF decreased slightly with increase in scratch length, which indicates that the Si/MoS\textsubscript{2} coating has a remarkable lubricating effect.

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