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DEVELOPMENT AND PERFORMANCE EVALUATION OF Ti-WS_2 SOLID ULTRA LUBRICIOUS COMPOSITE THIN FILM COATING BY PULSED DC CLOSED FIELD UN-BALANCED MAGNETRON SPUTTERING

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ABSTRACT

WS_2 based composite coating has been deposited on substrate of 40C8 mild steel disc having 25mm diameter and M2 grade HSS rectangular block using Pulsed DC Closed Field Un-balanced Magnetron Sputtering (CFUBMS) process. Improvement of the traditional WS_2 coating has been attempted by incorporation of Ti into soft matrix of WS_2. Preliminary investigation showed densification of the WS_2 matrix due to such modification. Coatings were characterized in detail using several physical and mechanical characterization techniques. Performances of coatings were evaluated using ball-on-disc test. Ti-WS_2 coating showed lower edge plane intensity of WS_2 in GIXRD spectra and highly dense structure and improved tribological properties along with higher adhesion and hardness compared to pure WS_2 coating. In ball-on-disc test the co-deposited WS_2-Ti coating showed lower ($\mu \approx 0.04$) and stable coefficient of friction at normal humid atmospheric condition and corresponding low wear over long period. This attempt is made to co-deposit WS_2-Ti composite coating to achieve superior properties compared to MoS_2-Ti composite coating using pulsed DC CFUBMS process. Here systematic investigation was conducted to identify the role of different process parameters influencing physical and mechanical characteristics of the coating. Several experiments were conducted by varying deposition pressure and WS_2 cathode power density. Tribological tests were conducted to evaluate the performance of the coating. The present investigation clearly reveals that low value of coefficient of friction is not only closely associated with orientation of the basal plane but also stoichiometric (S/W) ratio in the deposited film. It is observed that to obtain high deposition rate with favorable orientation of the basal plane parallel to the substrate surface as well as favorable stoichiometric (S/W) ratio, deposition has to be done at relatively high pressure.

KEY WORDS: Ti-WS_2 Solid lubricants, Thin film, Composite coating, Basal plane(002) Stoichiometric ratio, Magnetron sputtering, fractography, Tribology.

INTRODUCTION

Fundamental properties of MoS_2/WS_2 as Transition metal dichalcogenide (TMD) are, in many ways, a gift of the Nature to the mechanical engineers looking for friction reduction. TMDs exist in two crystal forms, hexagonal and rhombohedral. With hexagonal structure, which is the most common and important for low-friction applications. The hexagonal crystal structure with six-fold symmetry, two molecules per unit cell, exhibits a laminar, or layer-lattice structure. Each chalcogenide(S) atom is equidistant from three metal(Mo/W) atoms, end each metal atom is equidistant from six dichalcogenide atoms. The attraction between the metal and dichalcogenide atoms is due to powerful covalent bonding; however, there is only weak Vander Waals attraction between the lattice layers.TMD family consists of molybdenum, tungsten and niobium disulphides and diselenides. Tellurides $MeTe_2$ (Me — transition metal) are, technically speaking, members of the TMD family as well, but their low-friction behavior is questionable. To reduce friction, TMD is often used either as an oil additive or as a coating. Solid lubricant materials, such as graphite and MoS_2, have low coefficient of friction and good lubricity. The wear-resisting property of sliding part surface was improved by coating some solid lubricant materials on the surface. But some solid lubricant materials, especially MoS_2 will be obviously oxidized in high temperature. This will impact coating's lubricity and sticking with metal surface. The titanium was then used to deposit an interlayer, which led to an improvement in coating adhesion and load bearing capacity. A natural progression of this work led to incorporation of titanium into the coating itself resulting in improved friction and wear properties. These coatings are harder, much more wear resistant, and also less sensitive to atmospheric water vapour for terrestrial applications in normal atmosphere than pure MoS_2/ WS_2 coatings.

EXPERIMENTAL CONDITIONS: A: process, B: Pressure (mT); C: Duration(minutes); D: Targets and substrate power supply conditions @ 200kHz,60% duty cycle

Table:1 Experimental conditions

A	B	C	D
Target cleaning	1.5	10	(Ti) :1.0A, 400V (WS2) : 0.2A, 420V
Ti-ion etching	1.5	25	(Ti) :1.0A, 200V (WS2) : 0.2A, 403V Substrate bias -500V
Ti adhesion layer n	1.5	15	(Ti) : 4.0A, 255V (WS2) : 0.2A, 339V Substrate bias : -45V
C1 WS2+Ti	4.5	480	(Ti) : 0.4A, 265V (WS2) : 0.5A, 430V Substrate bias :-35V
C2 WS2+Ti	4.5	480	(Ti) : 0.4A, 315V (WS2) : 0.8A, 495V Substrate bias : -35V
C3 WS2+Ti	4.5	480	(Ti) : 0.4A, 245V (WS2) : 1.02A, 277V Substrate bias : -35V
C4 WS2+Ti	7.1	480	(Ti) : 0.4A, 275V (WS2) : 0.5A, 427V Substrate bias :-35V
C5 WS2+Ti	7.1	480	(Ti) : 0.4A, 275V (WS2) : 0.8A, 455V Substrate bias : -35V
C6 WS2+Ti	7.1	480	(Ti) : 0.4A, 255V (WS2) : 1.02A, 455V Substrate bias : -35V
C7 WS2+Ti	11	480	(Ti) : 0.4A, 265V (WS2) : 0.5A, 400V Substrate bias : -35V
C8 WS2+Ti	11	480	(Ti) : 0.4A, 270V (WS2) : 0.8A, 450V Substrate bias : -35V
C9 WS2+Ti	11	480	(Ti) : 0.4A, 235V (WS2) : 1.02A, 255V Substrate bias : -35V

TRIBOLOGICAL CHARACTERISTICS

Pin-on-disc tests were conducted to evaluate the performance of the coating. This test was carried out in ball-on-disc configuration in which, a WC ball(ϕ6mm) having hardness of 91HRA,was held against a WS_2-Ti coated mild steel disc with a dead load of 2N at normal humid atmosphere (55-60%). The disc was made to rotate at a surface speed of 10cm/s at that point of sliding. This test results clearly indicated a very low value of friction coefficient in the range of 0.03-0.04 when the deposition was done at very high pressure of 11mT and WS_2 cathode current of 0.8A.This low value of friction coefficient was found to be very sable and retained up to a sliding distance of 1200m. As it showed least and stable value of coefficient of friction.

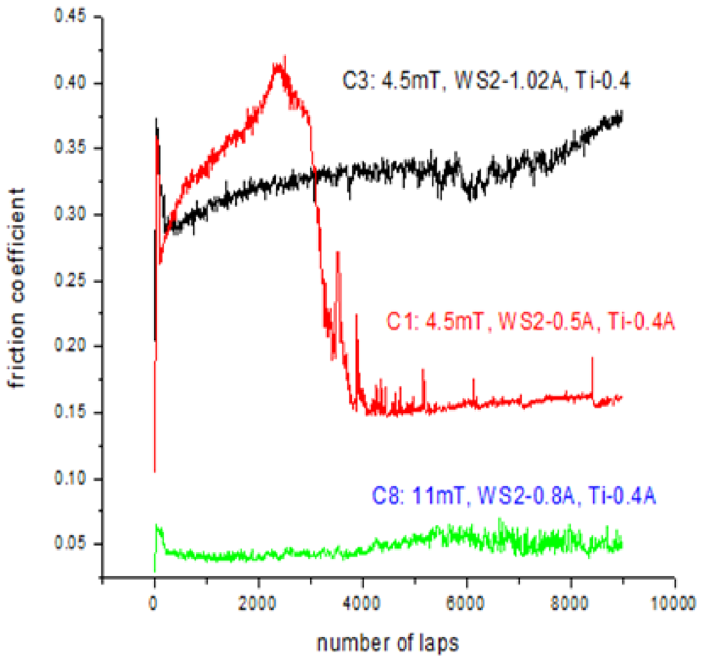

Fig.1) Comparison of variation in coefficient of friction for different coating architecture during ball-on-disc test

PHYSICAL CHARACTERIZATION

Surface morphology was observed for Ti-WS_2 composite coatings in FESEM and in SEM along with Energy dispersive spectroscopy analysis was done to understand the chemical composition. For the experimental conditions are given in Table, comparable study made for coating architectures C1,C3 & C8. SEM images of surface morphology and corresponding fractographic SEM images indicating thickness of the coating. Corresponding fractographic SEM images indicating thickness of thecoating. Coating architecture **C8** shows dense and compact coating. Thickness of the coating achieved during 8 hours of deposition appear to be around more than 3microns. From EDS analysis Ti atomic percentage and Stochiometric ratio (S/W) in the deposited film are significant factors for film growth rate, compact and dense structure. dense structure. significant factors for film growth rate, compact and dense structure. From EDS analysis Ti atomic percentage and Stochiometric ratio (S/W) in the deposited film are significant factors for film growth rate, compact and dense structure coating.Coating architecture **C8** shows dense and compact coating. Thickness of the coating achieved during 8 hours of deposition appear to be around more than 3microns. From EDS analysis Ti atomic percentage and Stochiometric ratio (S/W) in in the deposited film are significant factors for film growth rate, compact and dense structure. rate, compact and dense structure. rate, compact and dense structure. dense structure.

Table.2)Chemical composition observed in EDS for C8

O_2%	W%	Fe%	S%	Ti%	Total%
35	21	0.7	30	12	100

From EDS analysis Ti atomic percentage and Stochiometric ratio (S/W) in the deposited film are significant factors for film growth rate, compact and dense structure.

GIXRD ANALYSIS: Comparing with the JCPDS data file for WS2 it was observed that the major peak was WS2 basal (002) plane and the edge plane (102,103) intensity was less. Hence it can be said that the pure WS_2-based coating was mostly basal oriented. So the deposition parameter was such that it promoted basal oriented coating. All of the WS_2 peaks showed peak broadening i.e. in mathematical way a large value of FWHM (full width half maximum). Hence it can be deduced from Scherrer's formula that the crystalline size decreased (Scherrer's formula- *D*=0.9!/"*cos# where *D* is the crystalline size, ! the wavelength of Cu K!, " the full-width at half maximum (FWHM) of the diffraction peaks, and # the Bragg's angle). All of the WS2 peaks showed a tendency of left shift that is peak appeared at less value of 2". According to literature review it happened due to two reasons- 1)Sulphur vacancy in the WS2 lattice due to high bias and 2) Large compressive residual stress due to high bias with the incorporation of Ti it was seen that the oxide peaks became less frequent or the intensity reduced, which definitely showed increase in oxidation resistance.

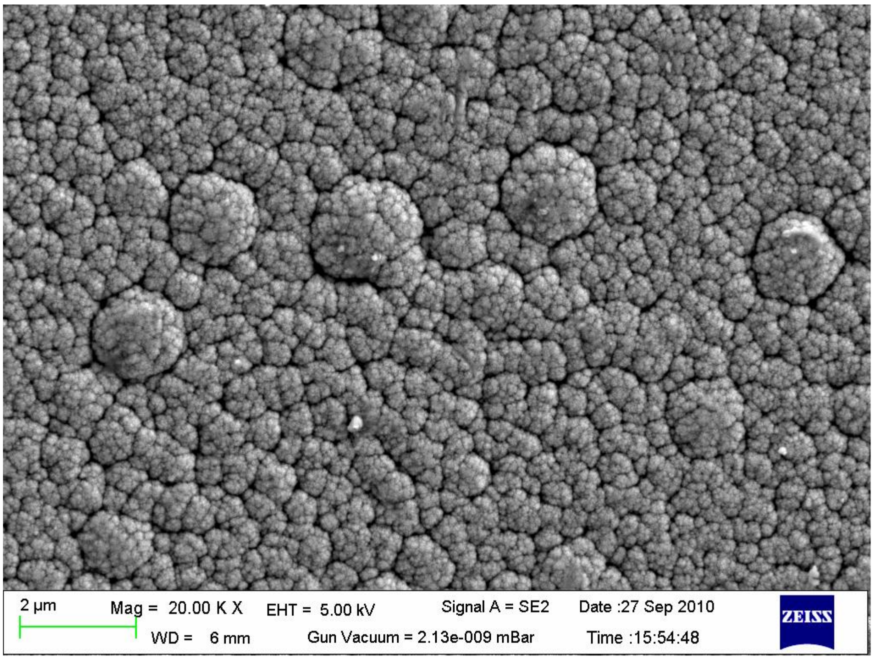

Fig.3) SEM for **C8**

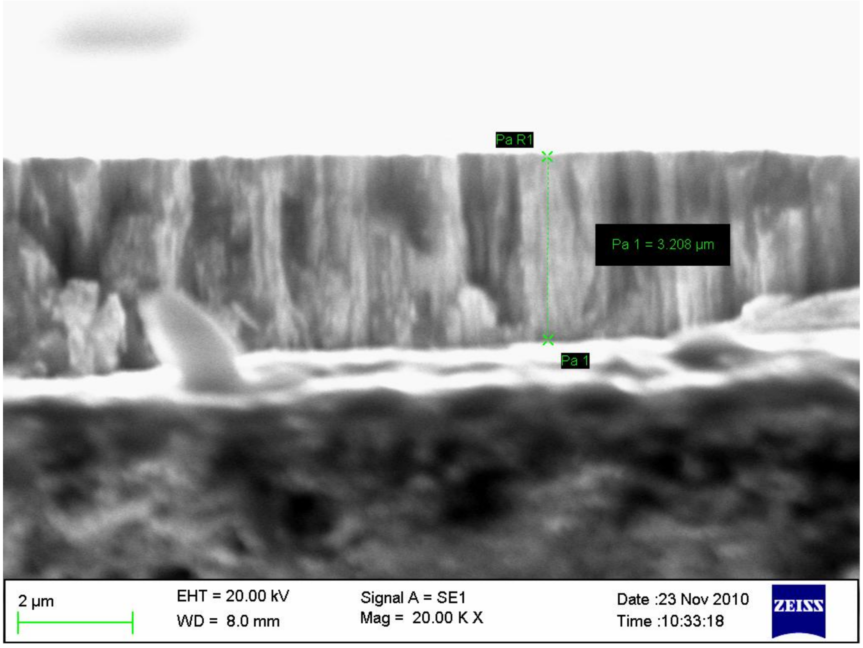

Fig.3) Fractographic view for **C8** : : 3.208µm

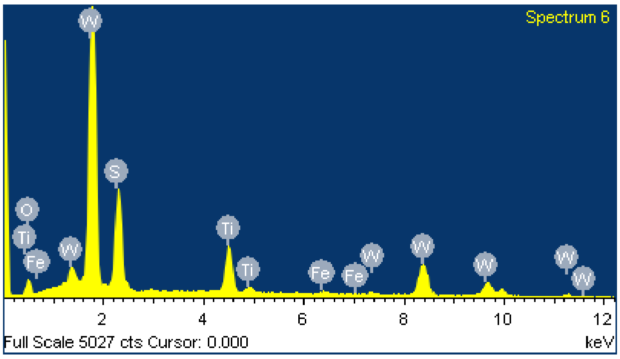

Fig.4) EDS analysis for C8

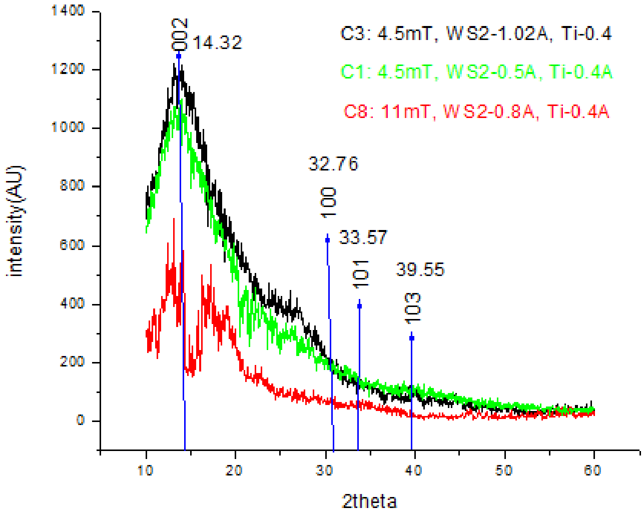

Fig.5) GIXRD spectrum for WS2-Ti composite coating

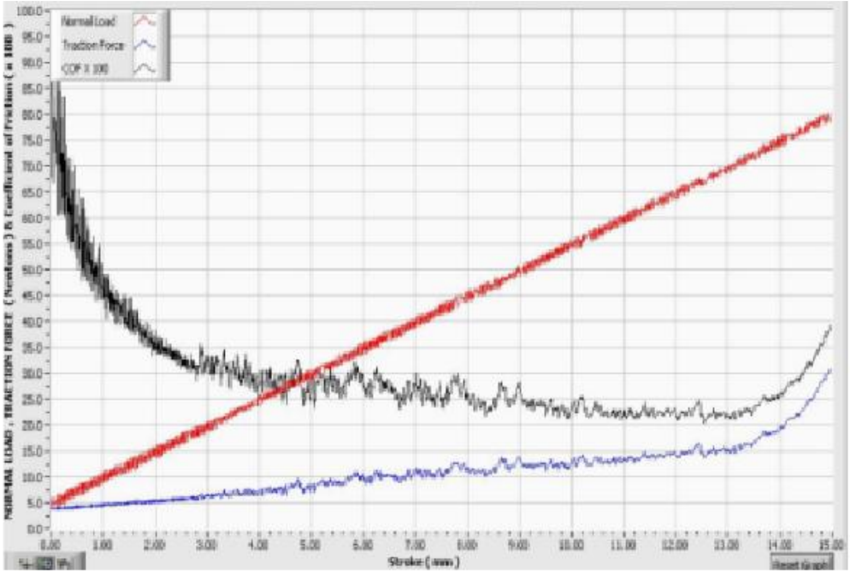

Fig.6) Adhesion evaluation by scratch test

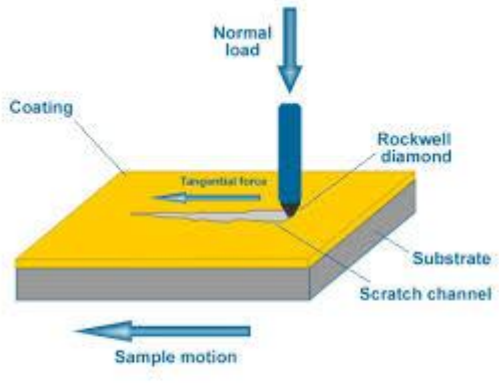

Fig.7) Adhesion scratch test.

In WS2-Ti spectrum there was no peak for free Ti or TiS_2. So it can be suggested that Ti atoms are segregated at the grain boundary of WS_2 or they are located between two WS_2 layers. This observation can demonstrate the amorphous nature of the composite coating. The existence of 002 basal plane parallel to substrate surface is also visible in fig.5, however the peak height and sharpness of the peak is found to be less, what can be seen for specimen C8 which indication of more Amorphous in nature of coating. This can be seen in SEM micrograph of C8

MECHANICAL CHARACTERIZATION

Scratch and indentation adhesion test: The adhesion of the coating was studied by a TR-101M5, DUCOM scratch tester. The scratch tests were performed with a Rockwell C diamond stylus (0.2 mm radius) drawn across the surface of the coating at a constant linear speed of 0.20mm/sec The normal load was varied linearly from 5 to 80N. Adhesion performance is usually quantified as the normal load required to delaminate the coating and is referred to as critical load “Lc”. This corresponds to the abrupt change in the friction or tangential force required to drive the diamond stylus across the coating. Hence, “Lc” was determined from the plot of friction force (or coefficient of friction) with respect to scratch length as provided by the software WINDUCOM, 2004 interfaced with the instrument. Three tests were done on each sample to confirm the critical load.

Micro-hardness test:

Vickers micro-hardness tests were carried out in order to determine composite film hardness using a LM-700 Digital Indentation Tester, LECO with a Vickers Indenter, LECO (standardized in accordance with ASTM E92). At least ten indentations were considered for each sample.

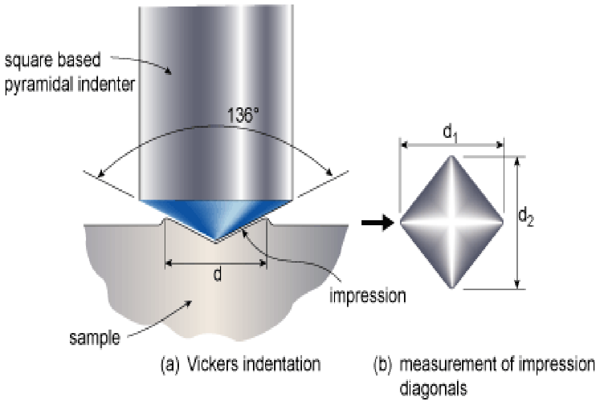

Fig.8) Micro indentation test.

$$HV=\{2PSin(\alpha/2)\}/D^2$$

P= load applied, in kgf, α=angle between the two opposite faces of diamond indenter, D=Mean diagonal of the indentation in mm

Value of Vicker’s hardness number observed to be less for high deposition pressure (C8,11mT) coating architectures because contribution of deposited film more than the substrate during the test.

RESULTS AND DISCUSSION

Table.3) Adhesion test results

Coating architecture	Critical load(N)
C1	69
C2	63
C3	40
C4	65
C5	30
C6	43
C7	75
C8	70
C9	75

In WS2 based coating cohesive failure started at very low load as evident from scratch track profile but complete de-lamination occurred at higher load. However the de-lamination is not sudden but gradual which can be seen from the Fig.6 The existence of Ti in the coating improved the adhesion. Probably this is due to gradual decrease of Ti when switching from Ti interlayer to WS2-Ti co-deposition. The existence of Ti throughout the coating also improved the adhesion. The low value of critical load (Pc) in C3 possibly due to low thickness of coating even the total deposition time was same as other cases. Critical load values during scratch adhesion test for high pressure (C8,11mT) coating architectures are considerably high.

Table.4) EDS analysis results

Coating architecture	Atomic% of Element			Stochiometric (S/W) ratio
	Ti	W	S	
C1	30.98	30.98	30.98	30.98
C2	22.81	22.81	22.81	22.81
C3	31.70	31.70	31.70	31.70
C4	28.49	28.49	28.49	28.49
C5	18.74	18.74	18.74	18.74
C6	24.15	24.15	24.15	24.15
C7	17.75	17.75	17.75	17.75
C8	12.00	12.00	12.00	12.00
C9	27.89	27.89	27.89	27.89

From EDS analysis Ti atomic percentage and Stochiometric ratio (S/W) in the deposited film are significant factors for film growth rate, compact and dense structure.

Table.5) Vicker's microhardness results

Coating architecture	Value of Vicker's hardness number(HV)
C1	1581
C2	465
C3	1190
C4	978
C5	859
C6	1103
C7	443
C8	593
C9	789

Value of Vicker's hardness number observed to be less for high deposition pressure (C8) coating architectures because contribution of deposited film more than the substrate during the test.

Table.6) Comparison of variation in friction coefficient (μ**)** for different architecture.

Coating architecture	μ
C1	0.262702
C2	0.154526

C3	0.330096
C4	0.08729
C5	0.04874
C6	0.201162
C7	0.193324
C8	0.047763
C9	0.1647

CONCLUSIONS

It is generally preferred to conduct deposition by sputtering at low process pressure for obtaining improved coating properties like high density, finer grain size, low residual stress. The coating of WS_2 deposited at low process pressure and low power density could show low value of coefficient of friction. However it is also observed that such a low pressure depositions of thin film of TMDs like WS_2 even at moderate cathode power density could affect the tribological property of coatings substantially. The coating deposited under such conditions exhibited a high coefficient of friction. In order to retain the excellent tribological property of WS_2 coating deposition process pressure had to be augmented along with the cathode power density. The coating architecture (C8) developed at high deposition pressure of 11mT showing better tribological performance during ball-on-disc test as coefficient of friction value of 0.04 which is significantly lower when compared to that of other architectures

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