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Tribological and Mechanical Behaviour of Molybdenum Thin Film Nanocoatings Prepared by Magnetron Sputtering

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Abstract: ***Coatings and surface engineering are used to protect manufactured components from thermal or corrosive degradation, impart wear resistance and hardness to the surface while retaining the toughness and ductility of the bulk component, also enhance the aesthetic and decorative appeal. In this work Molybdenum based ceramic Nanocomposite (MoSi2-SiC) coating was deposited on the surface of Mild steel substrate by Plasma Vapour deposition (PVD) Method in RF Magnetron Sputtering process. The thickness of the nanocoatings was varied as 50nm, 75 nm and 100 nm. X- ray diffraction (XRD) and Scanning electron microscopy (SEM) were used to characterize the microstructures of Mo based ceramic coating. The surface hardness of substrate and coating were determined using a Vickers microhardness tester. Corrosion resistance analysis was also carried out using acidic bath environment by weight loss method. The corrosion resistance of MoSi2-SiC coating was far better than that of substrate.***

Keywords: Nanocoating, Sputtering, Corrosion Resistance, SEM, MoSi2-SiC

1. Introduction

Physically vapor deposited (PVD) thin films are an industrially important class of materials which find use in a wide field of applications, from protective coatings in mechanical engineering for tooling and cutting operations [1], heaters [2] in electronic components, diffusion barrier coatings in energy devices [3–5], and optical applications in solar selective absorbers. Due to its superior physical and mechanical properties, Molybdenum based ceramic coating has found a wide range of applications, such as plasma faced components in fusion reactors. The objective of this work is to investigate the microstructural and corrosion behavioral properties of MoSi2-SiC coatings formed at different combinations such as 5%, 10%, 15% and 20% SiC with MoSi2 in reactive RF Magnetron sputtering process. The structural morphology of the coatings was explored by XRD, scanning electron microscopy (SEM) and the composition of the deposits was analyzed by energy dispersive X-ray analysis (EDX). The corrosion resistance of MoSi2-SiC coatings was evaluated by acidic bath method by dipping the mild steel substrate in different acid environment (H2SO4, HCL, and HNO3) with various concentrations such as 0.01N, 0.1N and 0.2N for 86.4ks in room temperature. The results reveal that the prepared ceramic nanocomposites are very good inhibitors with little concentration. The micro hardness of the coatings was determined by Vickers hardness apparatus with 0.1 kg load. Micro hardness values increased with CMC addition in the Mild steel.

2. Experimental Methods

2.1 Materials

The metal powders Molybdenum, Silicon, Carbon and chemicals sulphuric acid, hydrochloric acid and nitric acid were purchased from E-Merck and used as such. MoS_2 was used as lubricant for preparing NC pellets in Die set assembly. Double deionised water was used for all processes in corrosion studies.

2.2 Synthesis of Nanocomposites

The composite is prepared in three different elements with Molybdenum, Silicon and Carbon which forms MoSi2 as primary matrix and SiC as secondary matrix. In this present study, elemental powders of Mo (99.9%, 1-2µm), Si about 20µm and fine Carbon black (99.9%, 45 µm) are mixed in the desired proportions in a Glove box (Model: M Braun, AB Star-Germany) under argon gas atmosphere and sealed in a cylindrical WC vial together with 50 WC balls of 10 mm in diameter so as to obtain SiC of 5%, 10 %, 15% and 20 % by weight with MoSi2 powder composite. The ball milling experiments are carried out using high-energy ball mill (Model: Pulversitte 6, Germany) at a rotation speed of 300 rpm for 60 hrs of high temperature milling to attain the final by-product. [6]

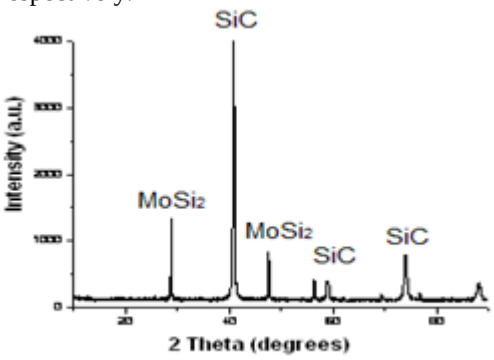
3. Microstructural analysis of Nanocomposite

3.1 XRD analysis

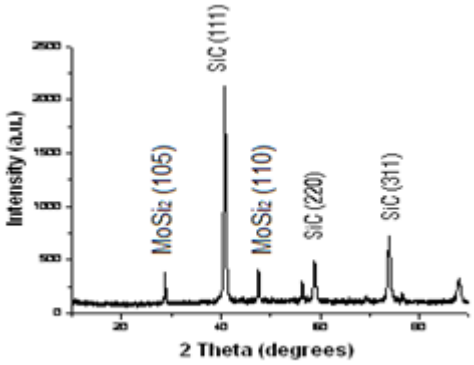
The XRD patterns of $MoSi_2$ & SiC NC are represented in Figure 1 (a-b) for two different combination of Nanocomposite such as 10% and 15% SiC with MoSi2. A single distinct peak appears at $2\theta = 41.4°$ which indicates the crystallinity of SiC that is resembled with JCPDS file No. 29-1129 (Naveen et al.,2010) and no other peaks appearing over the scan range from 30° and 45°. According to XRD pattern, the peaks corresponding to SiC are appeared additionally at $2\theta = 59.1°$ and 74.5° (Figure1). Also, from XRD pattern of the composites, the crystalline size of the samples is calculated using Debye Scherer equation (1).

$$D = \frac{0.9\lambda}{\beta \cos\theta} \quad (1)$$

Where λ is the wavelength of X ray radiation, θ is diffraction angle, β is angular width at half maximum intensity. The particle sizes are calculated based on eqn. (1) as 9.94 nm and 11.83 nm for 10 % and 15% SiC & MoSi2 combinations respectively.



(a) $MoSi_2$ -10 SiC

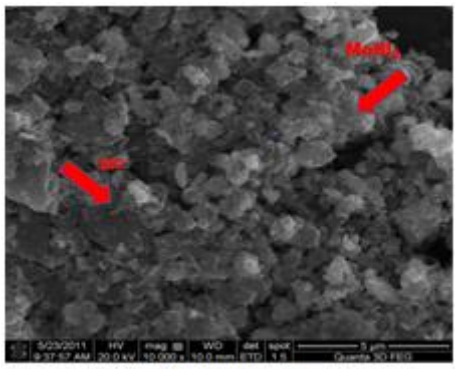


(b) $MoSi_2$ -15 SiC

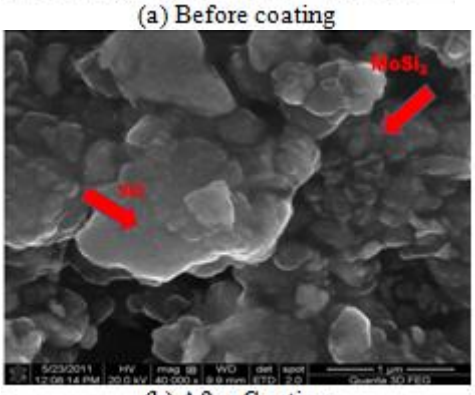
3.2 SEM/EDAX Analysis

Scanning Electron Microscopy equipped with energy dispersive X ray spectroscopy analysis (SEM-EDX PHILIPS XL 30) was used for investigation of microstructure and elemental analysis of the sample obtained at different conditions. The morphology of the synthesized MoSi2-SiC composite and different phases were observed by scanning electron microscopy. Figure 2(a-b) shows the SEM images of Nanocomposites in which MoSi2-SiC are identified as two flattened different phases. This is because of crushing the base powder along with secondary particles for prolonged time.

Figure 2(a) provides the image of MoSi2-10%SiC nanocomposite and represents clear visibility of individual powder particles. Figure 2(b) shows the SEM image of MoSi2-15%SiC composite powder which is milled in high energy ball mill for about 60 hrs. The increase in % of SiC by weight increases the particle sizes of composites because of constant milling time and hard nature of SiC.[10]



(a) Before coating



(b) After Coating

4. Corrosion Behavioral Analysis

4.1 Preparation of acidic medium

The mild steel plates are cut into small pieces of dimension 25mm x 25mm x 2mm and are dipped in pickling solution (5% H2SO4) for 5 minutes and washed with distilled water. After drying, the steel plates are cleaned, polished with various grades of emery sheets and degreased using acetone. The weight of the specimens with absence of ceramic coating were noted and then immersed in glass beaker containing test solution of various concentrations of sulphuric acid, hydrochloric acid and nitric acid (such as 0.5N HNO_3, 0.1N HNO_3 and 0.2 N HNO_3) separately for 24 hrs. After the time duration, the specimens were removed from the solution and washed thoroughly with distilled water and placed in hot oven for few minutes for drying. Finally the weight was measured. The differences in weight were noted and the percentages in weight loss (WL), corrosion rate (CR) and inhibition efficiency (IE) were calculated using eqs.

$$\%\text{Weight Loss} = \frac{w_i - w_f}{w_i} \times 100 \quad (2)$$

$$CR = \frac{87.6W}{DAT} \quad (3)$$

Where W, D, A and T are weight loss in mg, metal density in g/cm3, area of steel specimen in cm2, time of exposure of metal specimen in hrs respectively.

$$\%IE = \frac{W_a - W_p}{W_a} \times 100 \quad (4)$$

Where Wa and Wp are weight loss in g of m.s. in absence and presence of inhibitor respectively.

Table 1: Corrosion rate and Inhibition efficiency of Mild steel in ***0.05N acid solution*** *of 5% SiC-$MoSi_2$*

Coating Thickness (nm)	Weight Loss (%)			Corrosion Rate (CR)			Inhibition Efficiency (IE) %		
	H_2SO_4	**HCL**	**HNo_3**	**H_2SO_4**	**HCL**	**HNo_3**	**H_2SO_4**	**HCL**	**HNo_3**

0	0.480	0.050	0.060	1.736	1.240	1.480	-	-	-
50	0.180	0.020	0.040	0.794	0.490	0.992	54.280	80.000	95.250
75	0.160	0.017	0.032	0.744	0.420	0.793	57.140	99.650	98.640
100	0.05	0.005	0.009	0.248	0.130	0.223	85.710	99.870	99.880

Table 2: Corrosion rate and Inhibition efficiency of Mild steel in ***0.1N acid solution*** *of 5% SiC-$MoSi_2$*

Coating Thickness (nm)	Weight Loss (%)			Corrosion Rate (CR)			Inhibition Efficiency (IE)		
	H_2SO_4	**HCL**	**HNo_3**	**H_2SO_4**	**HCL**	**HNo_3**	**H_2SO_4**	**HCL**	**HNo_3**
0	6.880	0.370	0.480	30.000	1.736	1.190	-	-	-
50	2.820	0.340	0.390	12.400	1.488	0.960	58.670	14.280	78.250
75	2.270	0.220	0.210	9.920	0.992	0.520	66.940	42.850	82.140
100	1.700	0.188	0.140	7.680	0.843	0.340	74.380	51.420	88.140

5. Results and Discussion

5.1 Hardness Measurement

The Hardness value for uncoated mild steel is 122VHN and hardness value is increased from 142 to 168 VHN while increasing the coating thickness from 25 to 100 nm when coated with $MoSi_2$-5SiC. Similarly hardness value gradually increases for all the different combinations of ceramic nanocomposite coatings. It shows the hardness value of Mild steel coated with different ceramic nanocomposite for varying coating thickness. It predicts that hardness value is maximum for $MoSi_2$-5SiC with 100 nm coating thickness.

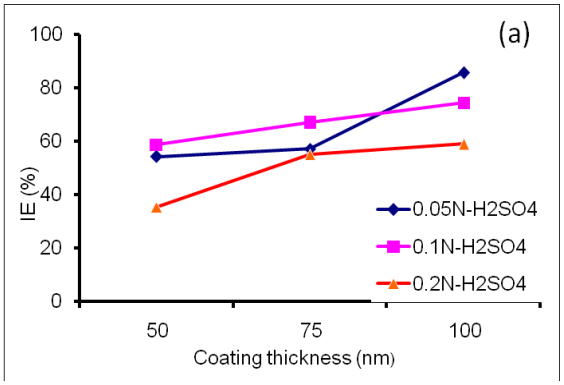
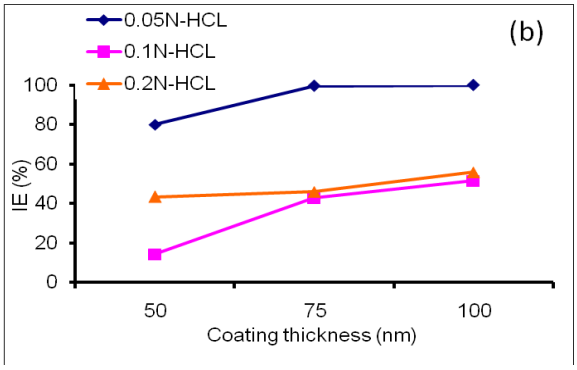
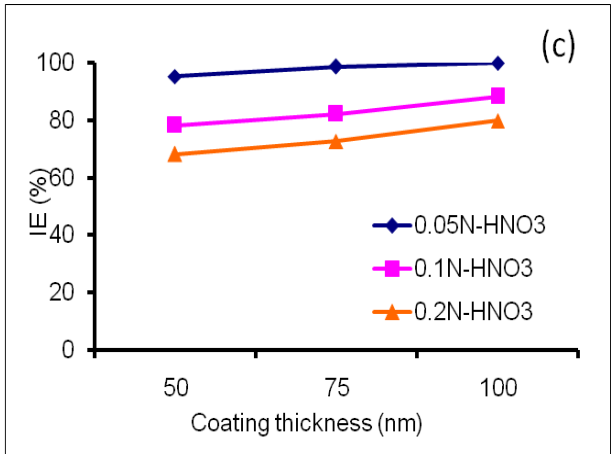


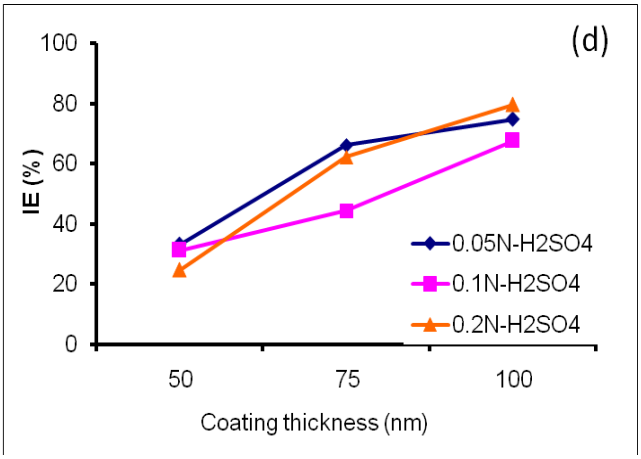
Figure 3: Corrosion inhibition efficiency of mild steel (a) $MoSi_2$-5SiC in H_2SO_4



(b) $MoSi_2$-5SiC in HCL



(c) $MoSi_2$-5SiC in HNo_3



(d) $MoSi_2$-10SiC in H_2SO_4

5.2 Corrosion of steel in acid medium by weight loss method

The corrosion behaviour of mild steel in various concentrations of acids H2SO4, HCL and HNo3 is tested by immersing at room temperature for about 24 hrs for different combinations of ceramic nanocomposite targets. In the presence of MoSi2-SiC coating, the ceramic coating is act as corrosion inhibitors. The weight loss in %, corrosion rate and inhibition efficiency are determined for various coating thickness. From the table it is clear that the inhibition efficiency is directly proportional to the coating thickness of the ceramic composites. Also weight loss is decreased while increasing the thickness of coating. Figure 3 predicts that Corrosion rate is indirectly proportional to coating material

thickness. The maximum corrosion inhibition efficiency is 85.71% for H2SO4, 99.87% for HCl and 99.88% for HNo3 for 0.05N concentration in 5% SiC-MoSi2 target.

6. Conclusion

Tribological behaviour of ceramic Nano composites coated on mild steel was investigated. The following conclusions were drawn from the study:

- Microstructural analysis reveal that while increasing the percentage of SiC by weight, the particle size of the nano composite also increases because of constant milling time of composites and hard nature of secondary matrix than primary matrix.
- Hardness value is maximum for MoSi2-5SiC with 100 nm coating thickness. Increasing the coating thickness from 25 to 100 nm micro hardness value increases, Also it gradually increases for all the combinations.
- It predicts that while increasing the coating thickness from 50 nm to 100 nm the corrosion inhibition efficiency of mild steel plate in sulphuric acid solution at 0.1 N concentrations is higher than 0.05N and 0.2N concentrations.
- In all the combinations the corrosion rate (CR) is gradually decreased from increasing coating thickness because of the influence of predominant nanocoating layer. Also the percentage in weight loss is reduced in decreased manner when the coating layer thickness is raised in all the cases.

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