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The effect of molybdenum (Mo) concentrations on the mechanical and magnetic properties of electrodeposited Co rich ternary CoMoW thin films from citrate electrolytic bath

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Cobalt–Molybdenum-Tungsten (CoMoW) alloy thin films were prepared through an induced electroplating route from a citrate bath on the surface of the copper electrode at the controlled value of pH 8. The CoMoW thin films have been prepared by varying the Mo concentrations like 0.1, 0.2, 0.3 and 0.4 M at a deposition time of 30 minutes over a plating current potential of 40 mA / cm2. The electrodeposited CoMoW coatings have been investigated with the help of Field Emission Scanning Electron Microscopy (FESEM), powder crystal X-ray diffraction (XRD), Electrochemical studies (impedance and polarization) and Vibrating Sample Magnetometer (VSM) to reveal its respective microstructure-based information, mechanical and soft magnetic nature of the synthesized CoMoW thin layers. The CoMoW thin films of an HCP crystal structure have been attained. The induced electroplated condition such as Mo concentration has a significant impact on the crystal structure system, surface morphology, and soft magnetic performances. The crystalline size of the CoMoW thin layers has varied from 22.66 nm to 42.87 nm. The synthesized CoMoW thin layers were smooth, without cracks and had uniform morphology. All the electroplated CoMoW films have the highest Co content along with low Mo content (Co content gradually decreased while increasing the Mo content in the deposits) and thickness varied from 10 to 20 µm. Through the electrochemical investigation studies, it is concluded that the corrosion rate of CoMoW thin films was slightly increased by increasing the Mo content and the corrosion resistance varied from 80.2 KΩ to 92.7 KΩ. The CoMoW thin alloy films with higher Co content exhibited a lower coercivity value of 3.69 Oe and the saturation magnetization of 49.049 emu /cm^2.

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Keywords: CoMoW coatings, Mo concentrations, Electroplating route, Thickness, Low coercivity and corrosion rate

1. Introduction

The modern electronic-based industries have undergone rapid advancement towards the utilization of thin alloy films. From the industrial point of view, the synthesis of magnetic thin films (cobalt-based alloy films) has obtained numerous real-time applications, including miniaturized electronic component-based devices like MEMS and NEMS devices. The important magnetic MEMS-based devices like micrometers, recording heads, and micro gears need the requirement of both hard and soft magnetic materials. Also, in the storage device applications domain, the magnetic thin coating plays a significant role and particularly the soft magnetic Co-based coatings have increased the efficiency of storage devices and microsensors. The inclusion of Mo with Co-based alloys may improve its soft magnetic behavior and it was decided to use Mo content. The presence of Mo content in the Co-based thin layers also enhances its mechanical

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properties like hardness and corrosion resistance. The Co-based alloy thin films can act as actuators in MEMS/NEMS due to their low coercivity along with higher magnetization values. An alloy like cobalt with molybdenum (CoMo) leads to the formation of an amorphous phase but the same alloy exhibits an enhanced soft magnetic nature and better corrosion behavior in the open environment. Based on the experimental conditions, the above said alloy may also exhibit the crystalline phase due to the addition of a third compound like Tungsten (W). There are many experimental routes available to fabricate the CoMo and CoMoW thin layer coatings among which the electrodeposition is the most appropriate method mainly for the synthesis of Co-based alloy thin films due to the advantages like cost-effective, synthesis from an aqueous medium, versatile, and easily film growth controllable process, etc., The operational bath conditions like electrolyte bath composition, pH, presence of additives and deposition rate potential. The modifications of electrodeposition parameters were shown to impact the microlevel growth structure, surface morphology and magnetic behaviors of the electroplated Co-Mo-based alloy thin film. Apart from the CoMo system, few research works were documented about the binary system like NiMo, FeMo etc., Among the various proposed Mo-based systems, incorporating Mo with Co gives the lower coercivity value [1 -2]. The percentage of cobalt in CoMo thin films will also play a crucible role to decide the magnetic type of CoMo thin films. The electroplated CoMo thin films may be transformed into hard magnetic nature while increasing the percentage of cobalt. The soft magnetic behavior of CoMo alloy films has been changed by introducing a small amount of metal-based third element like W in the proposed CoMo alloy thin films. To decrease CoMo thin layers' coercivity and maintain its higher value of saturation magnetization, it is planned to analyze the effect of W on the magnetic properties of CoMo thin layer coatings.

In addition to the better magnetic and corrosion behaviors, the CoMo alloy coatings would exhibit a higher reaction rate of hydrogen evolution (high HER) as matched with NiMo or CoW alloy coatings and due to the superior catalytic activity of CoMo coatings, it could be suitable for HER process. The CoMo mechanism is the best example of an induced co-deposition method since it is not possible to coat Mo alone through the electrodeposition route. It has been observed that the addition of a third element to CoMo thin films may significantly improve the electrochemical activities and stability which are essential for HER activities [3-5]. The mechanical-based functional properties like corrosion and hardness of CoMo thin films have been greatly enhanced by the influence of Zn (ZnCoMo) as compared to the pure zinc coatings and CoMo coatings [6 -11]. The present investigation mainly concentrates on the influence and effect of W in CoMo thin alloy films and the respective structural, mechanical & magnetic properties were documented.

2. Electrodeposition of CoMoW thin films from citrate bath.

The electrodeposition of Co-rich CoMoW thin alloy films has been achieved on the copper substrate by using a citrate bath containing the required starting compounds at variable Mo bath concentrations (varied from 0.1 M to 0.4 M – in the order of 0.1M). All the necessary chemical elements and plating bath details were listed in table 1. The electroplating bath of CoMoW was prepared using triple time distilled water by dissolving the desired chemicals in it. The pH value of the prepared citrate bath has been measured and it is found to be around 4. The measured pH value is adjusted to 8 with the help of ammonia solution. In this research work, Cu plate and stainless steel acted as a cathode and anode of customized size as 3 cm (breath) × 7 cm (length). Both electrodes have been exposed to the sequence of the substrate cleaning process and the process was initiated with a high-grade emery sheet followed by a detergent wash. In the second stage, the electrodes were well cleaned by using sulphuric acid (diluted) over a time of 3 minutes and finally cleaned with an ultrasonic sonicator to ensure the surface quality of the electrodes. The specific masking system was given to the cathode surface using adherent tape. Both electrodes were immersed in the prepared citrate bath and the current density was decided as 40 mA/cm^2 (bath temperature - 30˚C). The CoMoW thin layers were coated on the Cu surface with different Mo concentrations at 30 minutes of deposition time. Electroplated CoMoW thin layer coatings were undergone to several characterization systems like XRD, SEM-EDS, corrosion analysis, thickness measurement and magnetic measurements (VSM).

Metallurgical Microscope (make - Dewinter tech) and Vickers indenter (model - Shimadzu) were used to calculate the thickness and microhardness of the synthesized CoMoW thin films. The advanced D8 Bruker model (XRD pattern - LynxEye detector) has been employed to reveal the crystallographic details of coated CoMoW thin alloy films with the help of the Cu Kα series. The chemical elemental assessment and surface investigations have been executed using the FESEM-EDS (model - Jeol 6390LA/ OXFORD - accelerating voltage ranges from 0.5 to 30 kV - tungsten filament). The soft magnetic performance of CoMoW coatings was studied using the VSM model of Lakeshore - 7410S. The electrochemical analysis was performed using an inherent impedance analyzer (Auto-Lab with Potentiostat and Galvanostat).

Table 1. The necessary chemical elements and plating bath details of CoMoW thin alloy films.

Chemicals used & electroplating conditions	**Quantity (g / l)**
Cobalt sulfate	70
Sodium Molybdate	40
Ammonium citrate	70
Sodium Tungstate	10
Citric	10
Boric acid	10
pH value	8
Temperature	30˚C
Adjusted current density	40 mA / cm^2

3. Results and Discussions

3.1. Microstructural and Chemical elemental analysis.

The presence of chemical elements in CoMoW thin films has been analyzed using the EDS spectrum and the results are displayed in fig 1 and the corresponding atomic weight measurements are presented in table number 2. The obtained EDS results of CoMoW thin layers revealed the existence of cobalt, molybdenum along with tungsten contents and observed that the thin alloy film prepared at 0.1M concentration of Mo has very high cobalt content with very lower percentages of Mo and W contents. The CoMoW thin alloy films which have higher cobalt content have the best magnetic nature and at the same time, the presence of low W and Mo content leads to a better corrosion resistance value. It is also observed that the presence of Mo content gradually increased while increasing its source element concentration and at higher concentrations, the CoMoW film may have transitioned from crystalline phase to amorphous which may be due to the higher value of Mo content. The corresponding EDS mapping (fig 2) discovers the uniform orientation of Co, Mo with W all over the CoMoW coatings.

Table 2. EDS chemical analysis of electroplated CoMoW thin layers.

S. No	**Prepared sample details**	**Chemical elements name**	**Atomic weight percentage**	**Series type**
1	CoMoW (Mo – 0.1M)	Co	80.64	K-series
		Mo	12.15	L-series
		W	7.20	L-series
2	CoMoW (Mo – 0.2M)	Co	74.93	K-series
		Mo	18.98	L-series
		W	6.10	L-series
3	CoMoW (Mo – 0.3M)	Co	69.65	L-series
		Mo	24.97	K-series
		W	5.38	L-series
4	CoMoW(Mo – 0.4M)	Co	61.33	L-series
		Mo	36.03	K-series
		W	4.64	L-series

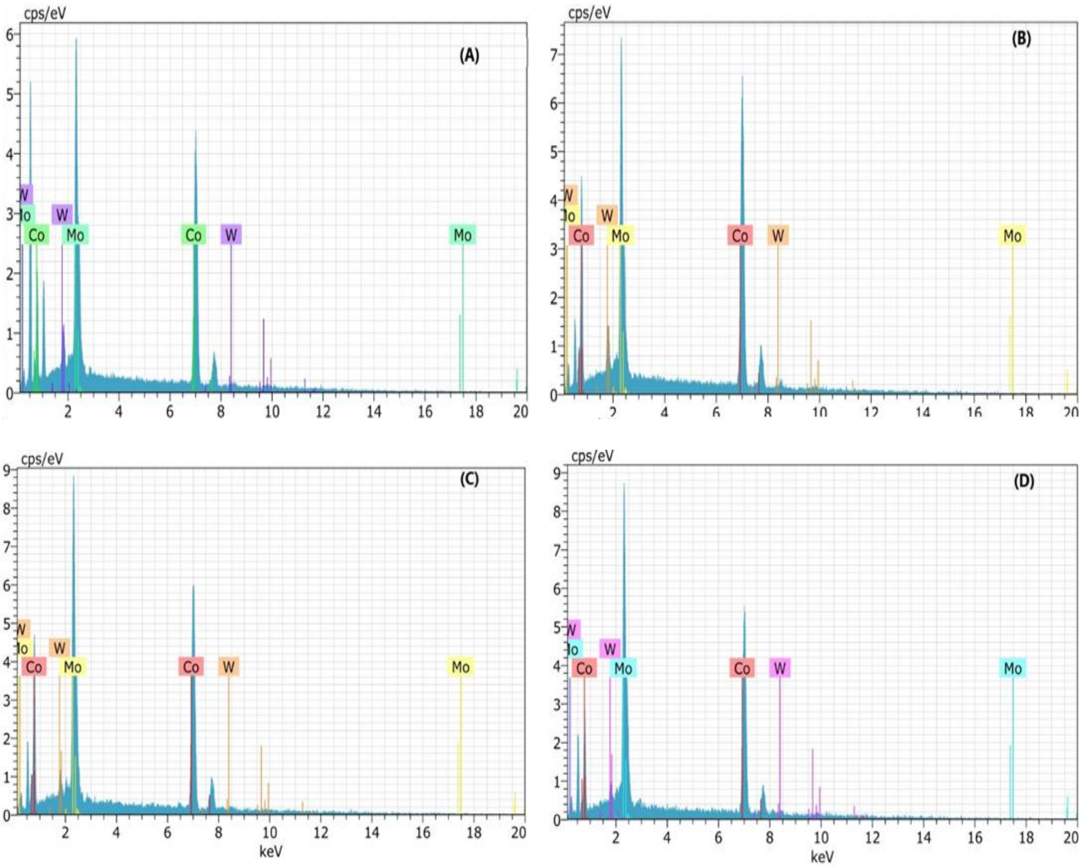


Fig. 1. EDS investigation of electroplated CoMoW thin layer coatings at concentration of Mo (a) 0.1M (b) 0.2M (c) 0.3M (d) 0.4M.

SEM investigation illustrates (fig 3) that the electrodeposited CoMoW thin alloy films have a bright and more uniform surface morphological structure without micro cracks, void gaps and pores. The CoMoW thin films coated at 0.1 and 0.2 M concentrations of Mo have visible and spherically shaped grain, including the uniform distribution of Co, Mo, and W grains as compared with CoMoW thin films coated at 0.3 and 0.4 M concentrations.

The obtained CoMoW films at 0.4 M concentration have a sheet-like structure due to the agglomeration of Co, Mo and W with each other which leads to enhancing the mechanical properties. The surface roughness value of CoMoW thin film is noticed by employing the profilometer and the coated CoMoW thin layers have the range from 165 to 171 nm as their roughness value. The roughness calculation tells that the CoMoW thin coatings at 0.1M (Mo) concentration have a slightly smaller surface roughness value than that of other obtained films.

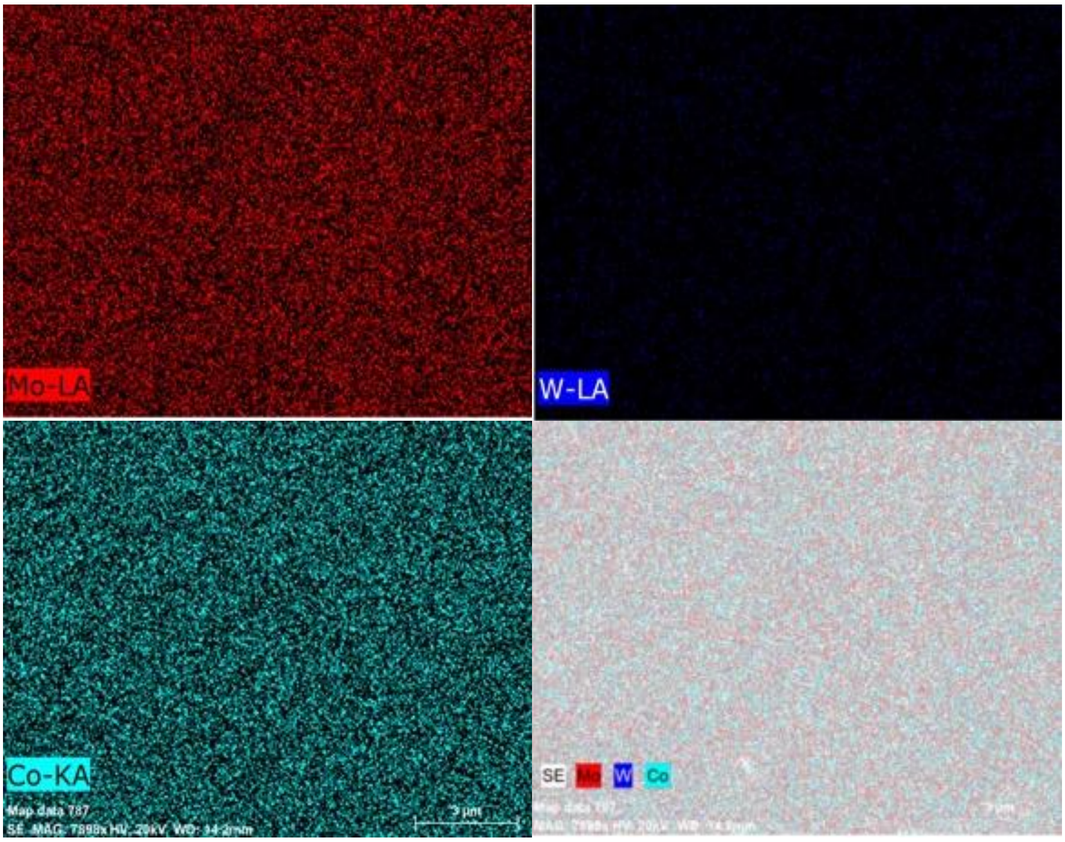
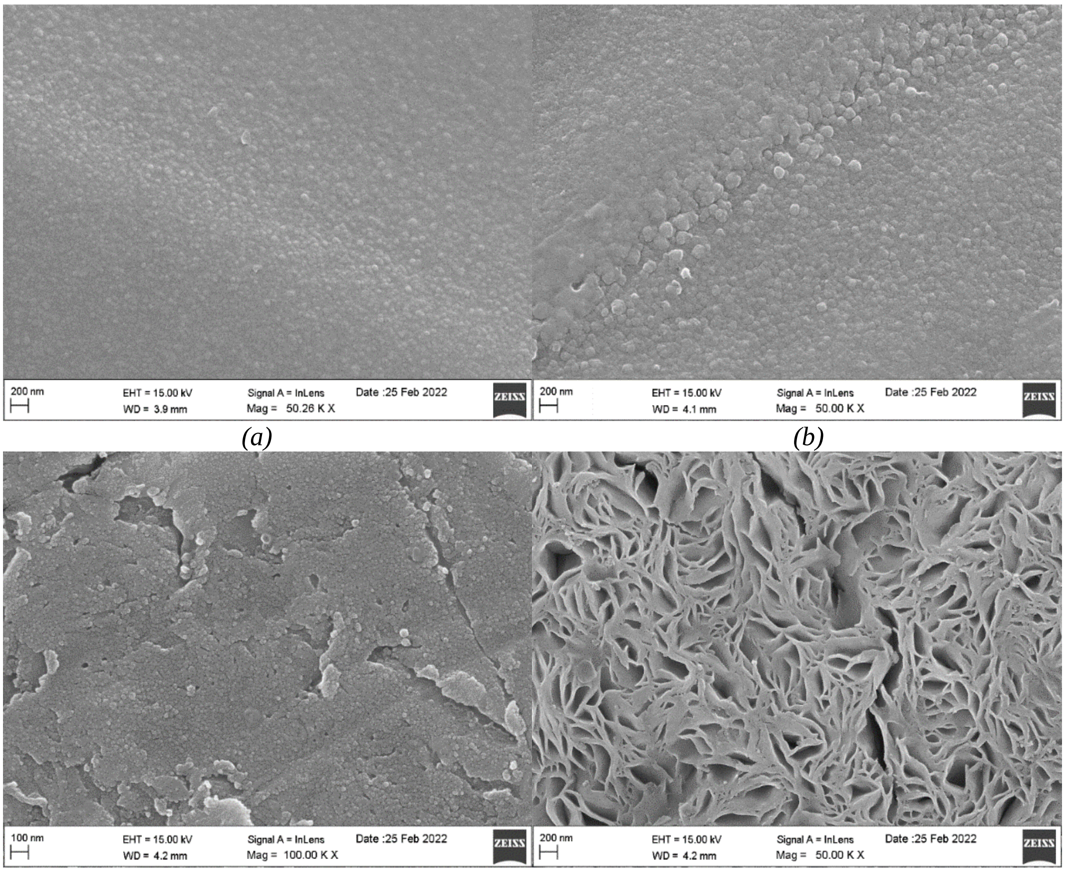


Fig. 2. EDS mapping of CoMoW thin layer coatings.

3.2. Structural studies – XRD results of CoMoW thin layer coatings

The existence of the crystalline nature of synthesized CoMoW thin alloy films has been assessed using a powder type diffractometer (PXRD) and the obtained graphs are shown in fig 4. The calculated structural dependent parameters of CoMoW thin layer coatings are described in table number 3. The resultant PXRD graphs of CoMoW coatings have been discovered the occurrence of four dominated sharp peaks about 2Ө values at 42.9, 51, 75 and 90 degrees (42.9 and 51 peaks link to cobalt diffraction and residual peaks to molybdenum and tungsten) which authorizes the development of single-phase CoMo solid solution with induced deposition of tungsten. The prepared CoMoW films have the crystal structure of HCP and the experimental details of XRD for CoMoW were matched with JCPDS (ICDD data). The CoMoW thin layer coatings at higher Mo concentrations have broad diffraction peaks instead of sharp peaks which reveals the occurrence of quasi–amorphous (mixed state of crystal and amorphous) phase.



(a) *(b)*

(c) *(d)*

Fig. 3. FESEM pictures of electroplated CoMoW thin layer coatings at concentration of Mo (a) 0.1M (b) 0.2M (c) 0.3M (d) 0.4M.

Table 3. Powder XRD results of electroplated CoMoW thin layers.

Name of the prepared samples	**"d" spacing value (Å)**	**crystalline size (D) (nm)**	**Estimated strain 10^{-3}**	**δ -dislocation density value (10^{14} / m^{-2})**	**Coating thickness (µm)**
CoMoW- (Mo - 0.1M)	2.113	22.66	1.4892	19.4685	11
CoMoW- (Mo - 0.2M)	2.103	27.45	1.2294	13.2705	10
CoMoW- (Mo - 0.3M)	2.203	42.87	0.7872	5.4412	14
CoMoW- (Mo - 0.4M)	2.202	46.20	0.7304	4.6833	20

The CoMoW thin films electroplated at 0.4M concentration of Mo content revealed the absence of sharp peaks as compared to the CoMoW films prepared at 0.1M concentration (presence of sharp peaks - without any additional impurity peaks) and it authorizes the transformation from perfect nanostructure system (due to the increases in Mo content) to semi-crystalline state.

Because the CoMoW thin film-coated at 0.4M concentration of Mo have the highest Mo content and it decides the crystalline nature of CoMoW thin layers. The particle size of CoMoW coatings was determined by using Scherrer's formula and presented the calculated particle size concerning the Mo concentrations is displayed in table 3. The particle size could be increased from 22.66 to 46.20 nm while increasing the Mo concentration from 0.1M to 0.4M.

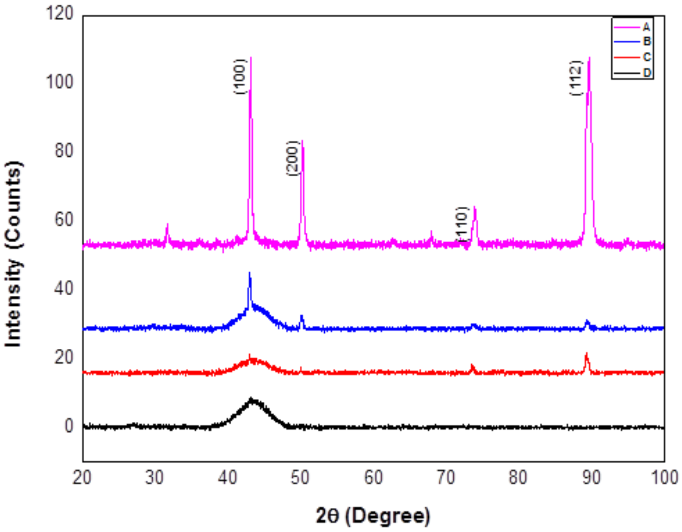


Fig. 4. P-XRD results of electroplated CoMoW thin layer coatings at various concentration of Mo (a) 0.1M (b) 0.2M (c) 0.3M (d) 0.4M.

3.3. Mechanical properties – Vickers microhardness of CoMoW thin films

The degree of adherence level for the CoMoW thin layer coatings onto the copper electrode (cathode) has been inspected using the scratch and bend tests. The CoMoW coated substrate plate was initially bent exactly to 180° and the same electrode was bent to its corresponding original position. The above-said process could be frequently repeated several times and concluded that the CoMoW thin layer coatings have significant adherence to the copper electrode.

Table 4. Microhardness and roughness of electroplated CoMoW thin layers.

Name of the prepared samples	**Hardness (VHN)**	**Roughness (nm)**	**Coating thickness (µm)**
CoMoW- (Mo - 0.1M)	284	165.34	11
CoMoW- (Mo - 0.2M)	289	166.41	10
CoMoW- (Mo - 0.3M)	291	170.80	14
CoMoW- (Mo - 0.4M)	298	171.02	20

The equally spaced lines have been drawn on the copper electrode (CoMoW coatings segment) by using a pin and soon after that process, an adhesive tape has been glued. Then, the pasted tape was carefully removed and it is evident that the CoMoW coatings have been strongly adherent to the copper substrate. The Vickers microhardness investigation of CoMoW thin layer coatings explored that the CoMoW film layer coated at 0.1M concentration of Mo has the hardness value of 284 VHN and found that the hardness values are slightly increased for CoMoW thin films coated at other concentrations (Mo). The experimental values of microhardness and thickness of CoMoW thin layers are listed in table number 4. The thickness of CoMoW thin films was calculated using a metallurgical microscope and the pictures are shown in fig 5.

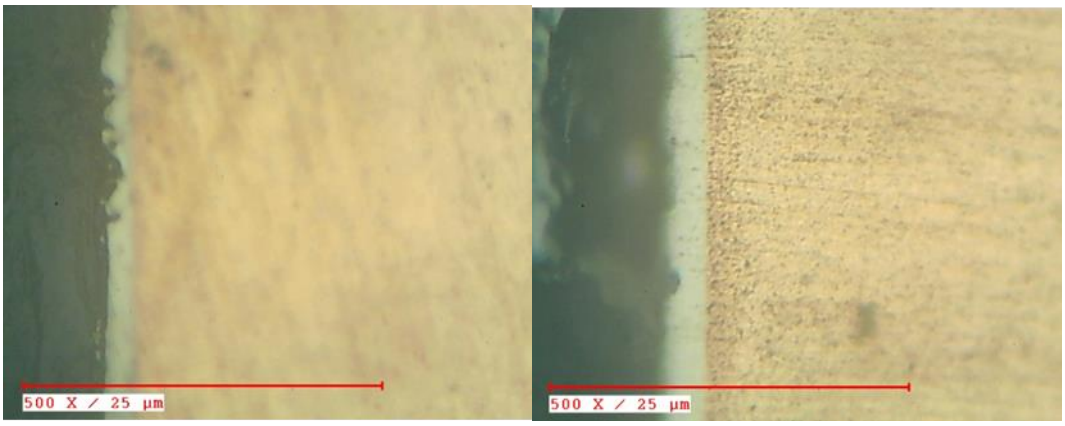


Fig. 5. Metallurgical microscope pictures of CoMoW thin layer coatings.

3.4. Mechanical characterization – Corrosion study of NiMOW coatings

The electrochemical (EIS) analysis such as polarization, impeadance etc., of CoMoW thin layers which are synthesized at various concentrations of Mo (0.1, 0.2, 0.3 and 0.4M) in a neutral pH medium were assessed using auto lab electrochemical workstation (AUT85670 model). In this current research work, a system of three electrodes was employed for the evaluation of CoMoW thin layer coatings on the copper surface. The platinum-coated narrow strip has proceeded as the counter-electrode, the CoMoW coated Cu electrode and the saturated calomel rod acted as working electrodes & reference electrodes respectively for the complete analysis. The impeadance measurements were accomplished in the range of frequencies between 0.1 Hz to 10 kHz with 10 mV as amplitude. The scan rate for the electrochemical studies has been retained as 0.02 V s^{-1}. The current responses (polarization analysis) from the CoMoW thin layers were recorded by keeping the potential values from 0 mV to −300 mV.

The Tafel plots for the electrodeposited CoMoW coated electrodes at different concentrations of Mo (a) 0.1M (b) 0.2M (c) 0.3M (c) 0.4M in the solution of neutral pH are displayed in fig 6.

The corrosive-based properties like corrosion potential, current density (E_{corr} and I_{corr}), slopes of Tafel graphs abbreviated as ba & bc and the polarization resistance (R_p) from the electrochemical experiments are documented in table number 5. The polarization graphs are the significant evidence and concluded that the corrosive potential tends to shift to a more positive (potential) side while increasing the concentrations of Mo content which enhances the corrosion resistance (R_p) value of the electrode coated with CoMoW (at 0.4M concentrations of Mo) due to the development of an effective barrier for neutral corrosive medium. Similarly, the corrosive current density (I_{corr}) values are drastically decreased while increasing the molybdenum (Mo) concentrations. The rate of corrosion for the CoMoW coated electrodes at 0.4M concentrations of Mo is 0.425 mm per year and found that the observed values are a lower rate of corrosion as compared to the other concentrations. As the Mo concentration increases from 0.1M to 0.4M, the Rp value starts to increase and it reaches the maximum resistance value at 0.4M concentration, causing the sheet-like microstructural morphology for the coatings of CoMoW. This can be strongly due to increases in Mo content from 12.15 % to 36.03% while raising the Mo concentration, which produces a sheet-like structure over the copper surface. During the polarization process time, the CoMoW deposited thin film acted as a strong barrier and effectively prevents the copper electrode from corrosion in the desired neutral medium. Thus, CoMoW deposited at 0.4M has a superior corrosion resistance (R_p) than that of CoMoW thin layers at other concentrations like 0.1, 0.2, and 0.3M, etc., The presence of W content also influences the corrosion resistance of CoMoW coated electrodes and even the film-coated at 0.1M also exhibited the better corrosion resistance of around 8.06 KΩ due to the influence of W content. The film-coated at low Mo concentrations also gives better magnetic properties and it could be useful for the MEMS-based device fabrications.

The obtained Nyquist graphs for the CoMoW coated electrodes at various Mo concentrations in the neutral pH solution are provided in Fig 6. The impedance values like charge transfer capability (resistance) calculated from the Nyquist graph are expressed in table number 5. The Nyquist graphs are the significant evidence and concluded that the charge transfer resistance tends to increase while increasing the concentrations of Mo content and has a maximum rate of R_{ct} at 0.1M concentration is around 940 ohms. As the concentration of Mo content increases the strength of the CoMoW coated thin film on the Cu increases and drops the system of a double layer formation by the CoMoW and the copper surface. Thus, the R_{ct} (charge transfer resistance) increases, hence through the redox response, charge transfer between cathode and anode is delayed and the substrate gets protection against the corrosion process.

Table 5. Polarization and Impedance data of NiMoW thin coatings coated at different duration.

Name of the prepared samples	**ba (V/dec)**	**bc (V/dec)**	**-Ecorr, Obs (V)**	**Icorr (A/cm^2) E-05**	**Corrosion rate (mm/year)**	**Polarization resistance (KΩ)**	**Charge transfer resistance (Ω)**
Mo - 0.1M	0.204	0.177	0.453	95.4	11.08	8.069	91.8
Mo - 0.2M	0.226	0.137	0.381	16.7	1.939	8.314	213
Mo - 0.3M	0.567	0.206	0.389	10.7	1.246	9.015	238
Mo - 0.4M	1.636	0.625	0.362	3.66	0.425	9.778	340

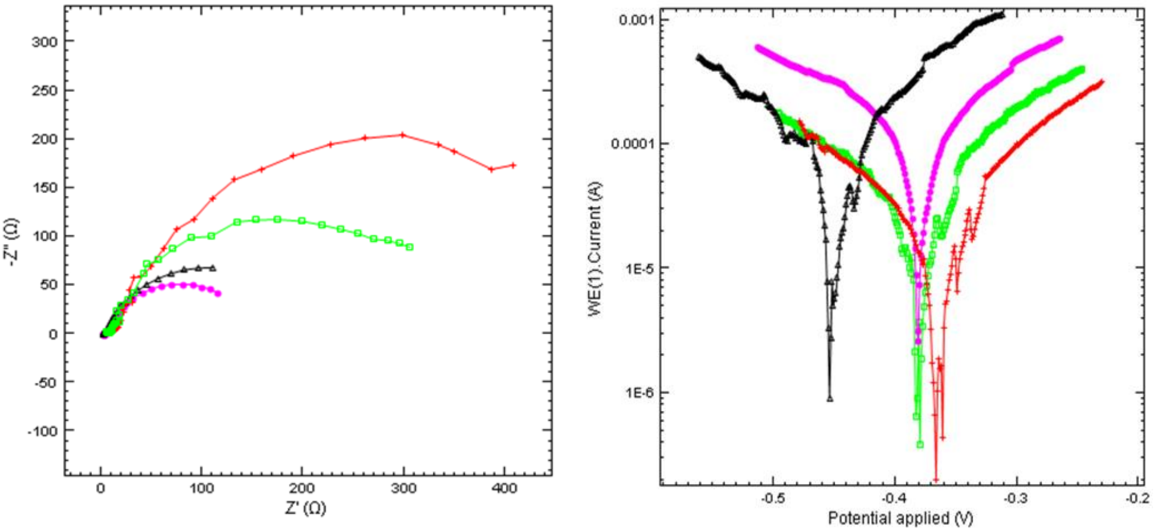


Fig. 6. Nyquist and Tafel plots of electroplated CoMoW thin layer coatings at various concentration of Mo (a) 0.1M (b) 0.2M (c) 0.3M (d) 0.4M.

3.5. Magnetic properties – VSM studies of CoMoW coatings

The magnetic nature of the electrodeposited thin CoMoW alloy films has been examined using the VSM instrument and their respective graphs are described in fig. 7. The observed (experimentally) magnetic values like saturation magnetization, retentivity, coercivity, etc., are recorded in table 6. The room temperature VSM analysis exposes that the CoMoW thin films exhibited a soft magnetic nature and the CoMoW thin layer coatings fabricated at 0.1M concentration of Mo content showed the excellent soft magnetic behavior of much lower coercivity of 3.691 Oe and 49.049 emu/cm^2 as the higher saturation magnetization. From the results of EDS, the reason for this better soft magnetic category is owing to the existence of higher Co content and the perfect nanocrystalline phase in CoMoW thin layers. The soft magnetic nature may be owing to the coherent allocation of cobalt, tungsten and molybdenum crystallites.

Table 6. Magnetic properties of CoMoW thin layer coatings.

Sample details	Coercivity Oe	Magnetization (Ms) emu/cm^2	Retentivity (Mr) emu/cm^2	Squareness
Mo - 0.1M	3.691	49.049	35.21	0.0089
Mo - 0.2M	41.83	37.584	521.53	0.0139
Mo - 0.3M	55.056	22.202	237.79	0.0172
Mo - 0.4M	67.84	17.797	195.52	0.0087

The CoMoW thin layer coatings which are fabricated at 0.2M concentration of Mo content reveal the occurrence of ferromagnetic nature but the obtained coercivity is marginally high (41.83 Oe). The CoMoW coatings obtained at 0.3 and 0.4M concentrations the higher coercivity and lower saturation magnetization. This is mainly owing to the presence of a mixed phase of the amorphous and crystalline system and also due to the decrease in Co content (increase in Mo content). For the higher concentrations of the Mo category, the Co content is decreased from 80.64 to 61.33 atomic percentage with W content of 4 to 5 percent. The occurrence of single-phase nanostructured solid solution of CoMo with induced deposition of W. The CoMoW thin films coated at 0.1M concentration of Mo content would have an excellent soft magnetic behavior which is a fundamentally needed character for the MEMS or NEMS based device fabrication industries. The VSM studies indicate that the achieved squareness value of CoMoW thin layers prepared at various Mo concentrations varied from 0.0089 to 0.0712. Finally based on the VSM studies, it may be determined that the CoMoW coated thin films showed the presence of a system of single domains. The Co, W, and Mo crystal grains have been subjectively distributed in the easy direction of magnetization.

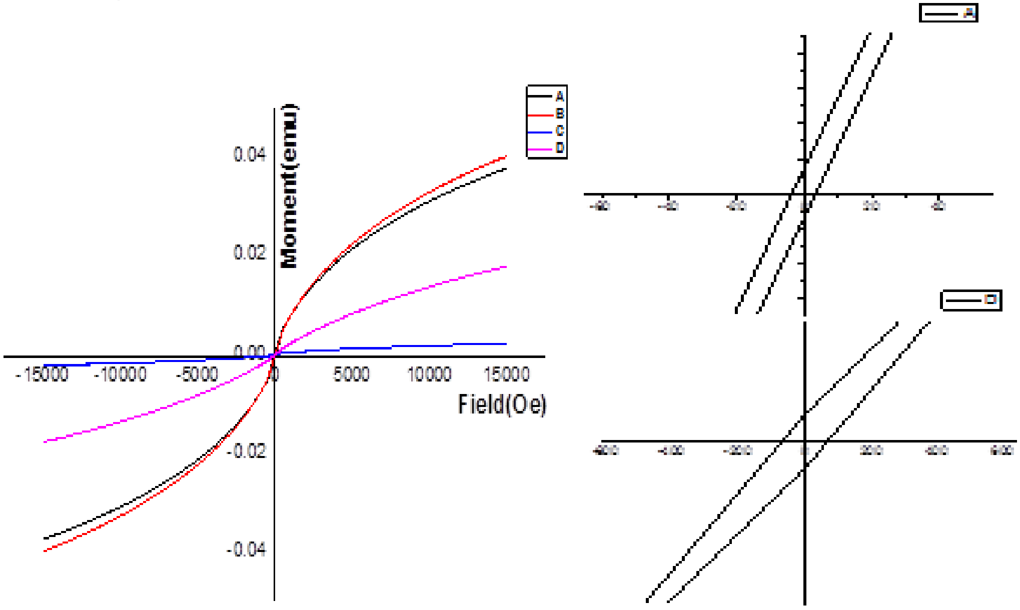


Fig. 7. Hysteresis loops of electroplated CoMoW thin layer coatings at various concentration of Mo (a) 0.1M (b) 0.2M (c) 0.3M (d) 0.4M.

4. Conclusions

W induced deposited CoMo thin layer coatings were fabricated on the cathode surface (substrate) using the electrodeposition route at a steady current density value of 40 mA/cm^2 by varying the Mo concentrations. The average calculated crystalline size of CoMoW thin layers varied from 22 to 46 nm. All the fabricated CoMoW thin alloy layers have a hexagonal (HCP) crystalline structure and the manufactured CoMoW thin layers have a uniform micro surface morphology along with nanoclusters of spherical shape and sheet-like structures with the absence of microcracks, discontinuity, and pores. The CoMoW coatings at 0.4M concentrations of Mo content have a higher resistance value against corrosion but the coercivity value is slightly high with a moderate magnetization value. This is primarily due to the existence of mixed-phase and the lower content of Mo with higher content of Co. The coating thickness of CoMoW thin layers has been found that it varied in the range between 10 to 20 μm and the CoMoW films are effectively adherent with the copper substrate (Cu). The CoMoW films at low Mo concentration showed enhanced soft magnetic properties with a very low coercivity of around 3 Oe and this may owe to the higher Co content and lower Mo percentage. It may be concluded that, as a result of this research work, the CoMoW thin alloy films coated at 0.1M concentration of Mo content are suggested for massive industrial device fabrications based on their excellent corrosion resistance, hardness and soft magnetic properties.

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