

Study on Properties of Polytetrafluoroethylene Doped CoMoP Alloy Films Prepared by Plating Method

Kangchen Shao*, Hongyuan Shi

College of Aeronautical Materials Engineering, Xi'an Aeronautical Polytechnic Institute, Xi'an, Shanxi, 710089, China

*E-mail: shaokangchennano@126.com

Received: 23 September 2021 / Accepted: 3 November 2021 / Published: 6 December 2021

Polymer PTFE was added into the plating bath to prepare CoMoP/PTFE by plating method. Deposition rate, thickness, friction coefficient, magnetic performance and corrosion resistance of CoMoP/PTFE alloy film was investigated. PTFE is a kind of polymer materials with lower friction coefficient and higher impedance. The PTFE doped in the CoMoP/PTFE could greatly increase corrosion resistance and magnetic performance. The CoMoP/PTFE alloy film obtained from the bath with 15 g/L PTFE has lower friction coefficient, optimal corrosion resistance and great magnetic performance. Surface morphology of the CoMoP/PTFE alloy film is a kind of typical nodular particles. PTFE is beneficial to reduce grain size of CoMoP/PTFE resulting in denser surface morphology. However, excessive PTFE in the plating bath tends to agglomerate resulting in the decrease of deposition rate and deterioration of film quality that contribute directly to the decrease of corrosion resistance and magnetic performance.

Keywords: Polymer PTFE; Plating method; CoMoP/PTFE alloy films; Corrosion resistance

1. INTRODUCTION

With the rapid development of electronic industry, electronic components are becoming miniaturized, intelligent and integrated. For the traditional motor and machinery industry, the bulk magnetic materials can be properly processed to meet the requirement of industrial applications. However, for microelectronic systems, magnetic films on micron scale with good magnetic and corrosion resistance performance are required. Magnetic films can be divided into permanent magnetic film and soft magnetic film.[1-3] Meanwhile, permanent magnetic film possesses high coercivity which is widely used in the micro motor field. Soft magnetic film with high permeability is widely used in thin film magnetic head, magnetic recording and other fields.

Because cobalt metal has the advantage of high hardness, good wear resistance and optimal

tensile strength, it is found out that Co based alloy films possess excellent mechanical performances. In addition to these advantages, the most important is that Co based alloy films have outstanding magnetic properties, which can not only be used as a medium for magnetic recording, but also can replace micro magnets in electronic devices. Therefore, Co based alloy films have become the focus of scientific research. For example, CoW alloy films with good mechanical and magnetic performance were reported by many researchers.[4-5] According to many literatures, CoMo alloy films with excellent properties can be prepared by plating or electroless deposition method.[6-7] CoNi alloy films with excellent soft magnetic properties were usually prepared and investigated.[8-10] Moreover, CoPtW and CoNiMn alloy films with higher coercivity were also widely reported in the literatures.[11-12] Although Co based alloy films possess excellent mechanical and magnetic performances, the corrosion resistance is not good enough. Therefore, many metal or nonmetal elements are doped into the Co based alloy films to greatly improve the corrosion resistance. CoW/SiC composite films with good anticorrosion performance were reported.[13-14] It was found out that corrosion resistance of Co based alloy films could be improved effectively by doping Al_2O_3 . [15-16] Moreover, some researchers also reported that phosphorus is beneficial to improve corrosion resistance.[17-18] Except for metal or nonmetal particles, polymer materials possess good chemical stable and outstanding corrosion resistance that are considered as a kind of innovative materials to improve performance of Co based alloy films. Polytetrafluoroethylene (PTFE) is a typical polymer with excellent corrosion resistance in acid and alkali solution. Therefore, polymer PTFE is added in the bath to prepare CoMoP/PTFE composite alloy films by plating method in the paper. Effects of PTFE concentrations on deposition rate, thickness, friction coefficient, magnetic performance and corrosion resistance of alloy films were investigated.

2. EXPERIMENTAL

CoMoP/PTFE alloy films were electrodeposited from the bath with different concentrations of PTFE from 0 g/L to 20 g/L. Specific information about the electroplating solution is listed in Tab.1.

Table 1. Plating solution of the CoMoP/PTFE alloy film

Chemical Reagent	Concentration/ g/L
$CoSO_4 \cdot 7H_2O$	30 g/L
$Na_2MoO_4 \cdot 2H_2O$	10 g/L
H_3BO_3	30 g/L
$NaH_2PO_2 \cdot H_2O$	10 g/L
$C_6H_5Na_3O_7$	80 g/L
Nano PTFE	0~20 g/L
$C_{12}H_{25}SO_4Na$	0.2 g/L

$CoSO_4 \cdot 7H_2O$ and $Na_2MoO_4 \cdot 2H_2O$ are the main salts in the plating solution to provide cobalt

and molybdenum for CoMoP/PTFE alloy films. $\text{NaH}_2\text{PO}_2 \cdot \text{H}_2\text{O}$ is selected to offer phosphorus. $\text{C}_6\text{H}_5\text{Na}_3\text{O}_7$ is considered as the complexing agent. H_3BO_3 and $\text{C}_{12}\text{H}_{25}\text{SO}_4\text{Na}$ are designed as buffering agent and surfactant respectively. The polymer nano PTFE is added in the plating solution to study the influence of PTFE on the performance of CoMoP/PTFE during the electrodeposition process.

Copper sheet (2 cm×3 cm) acts as cathode and platinum sheet (3 cm×3 cm) acts as anode in the plating process. Pretreatment is needed before the plating process. Copper sheet substrate is polished firstly by the polishing machine. Then, pickling (10% diluted hydrochloric acid) and alkaline (2% sodium hydroxide solution) cleaning are carried out in sequence. Ultrasonic wave (60 W, 40 kHz) is used to vibrate the PTFE solution to reduce the agglomeration effect of nano particles. The plating process lasts for one hour in the 100 ml solution at 60 °C using continuous mechanical agitation.

The thickness of CoMoP/PTFE is tested by surface profiler (KLA-P170) with sampling rate 100 Hz and scan size 3000 μm at scan speed 100 $\mu\text{m}/\text{s}$. Friction abrasion testing machine (HSR2M) is used to test the friction coefficient of samples. The length of wear mark is 10 mm with 10 N force for 5 min. Corrosion resistance of CoMoP/PTFE alloy films are evaluated by polarization curves based on corrosion current in 3.5% sodium chloride. Meanwhile, CoMoP/PTFE with 1 cm×1 cm size acts as cathode while platinum plate with 3 cm×3 cm size acts as anode. Saturated calomel electrode is chosen as reference electrode. The scanning potential is from -0.55 V to -0.45 V at 3 mV/s scanning rate. The electrodeposition rate is calculated by measuring the weight gain of the substrate after electroplating using a high precision electronic balance (FA2204B). Vibrating sample magnetometer (Lakeshore 7300) is used to test the magnetic performance of CoMoP/PTFE films based on coercivity and saturation magnetization. The surface morphology of samples is observed by scanning electron microscope (Hitachi S5000).

3. RESULTS AND DISCUSSION

3.1 Effect of PTFE on deposition rate and thickness of CoMoP/PTFE alloy films

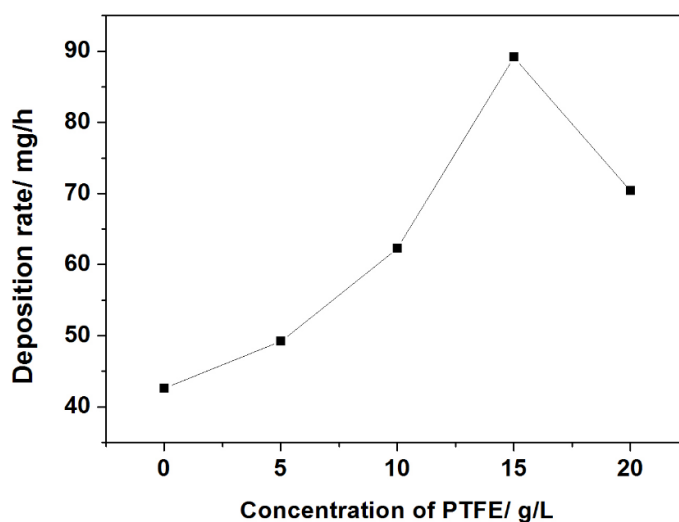
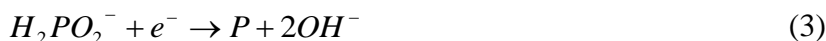
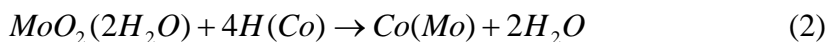
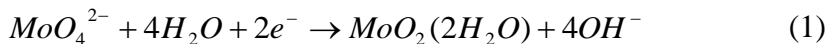


Figure 1. Effect of PTFE on deposition rate of CoMoP/PTFE alloy films; Copper sheet is cathode and platinum sheet is anode in the plating process. Concentration of PTFE is from 0 g/L to 20 g/L;

Different concentrations of PTFE range from 0 g/L to 20 g/L are added into the plating solution to prepare CoMoP/PTFE alloy films. The electrochemical deposition mechanism is as followings:[19]



Because molybdenum cannot be directly electrodeposited from the aqueous solution, the deposition process of Co and Mo belongs to a kind of inductive codeposition. It is found out that, under the catalytic action of the initial hydrogen on cobalt surface, molybdenum can be codeposited with cobalt, so as to obtain CoMo alloy films. Moreover, nano PTFE particle can easily enter the grain boundary and lattice of CoMo alloy to form CoMoP/PTFE alloy films with the action of electric field and stirring.

From the result of Fig.1, it is found out that PTFE in the bath can affect the deposition rate of CoMoP/PTFE alloy film. Increasing the concentration of PTFE in the plating solution is conducive to improving the deposition rate of the alloy film. When the concentration of PTFE keeps at 15 g/L, maximum deposition rate could be achieved around 90 mg/h. With the action of electric field and stirring, nano PTFE particles enter into the grain boundary and lattice of the alloy film to increase surface activity resulting in the increase of deposition rate. However, the deposition rate decreases when the concentration of PTFE in the bath is greater than 15 g/L due to the agglomeration phenomenon of suspended PTFE particles on the substrate surface. Same relationship between PTFE concentration and deposition rate is also reported in some literatures. [20-22]

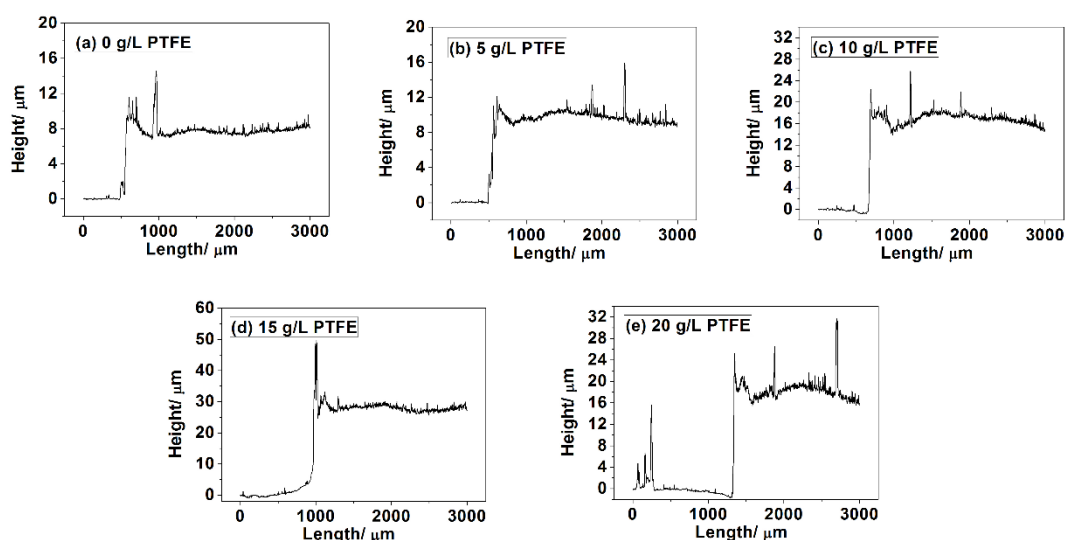


Figure 2 Effect of PTFE on thickness of CoMoP/PTFE alloy films, (a) 0 g/L PTFE; (b) 5 g/L PTFE; (c) 10 g/L PTFE; (d) 15 g/L PTFE; (e) 20 g/L PTFE; Scan speed 100 $\mu\text{m/s}$; Sampling Rate 100 Hz; Scan size 3000 μm ; Applied force 2 mg; Resolution 0.0391 A;

Fig.2 gives the thickness of each alloy film prepared from the bath with different

concentrations of PTFE. With the increase of PTFE concentration, thickness of the alloy film increases gradually and then decreases. The CoMoP/PTFE alloy film with maximum thickness could be obtained at the condition of 15 g/L PTFE. Nano PTFE is beneficial to increase the deposition rate that contributes directly to the increase of film thickness. However, excessive PTFE will cause serious agglomeration phenomenon resulting in a decrease in deposition rate and film thickness.

3.2 Effect of PTFE on friction and magnetic performance of CoMoP/PTFE alloy films

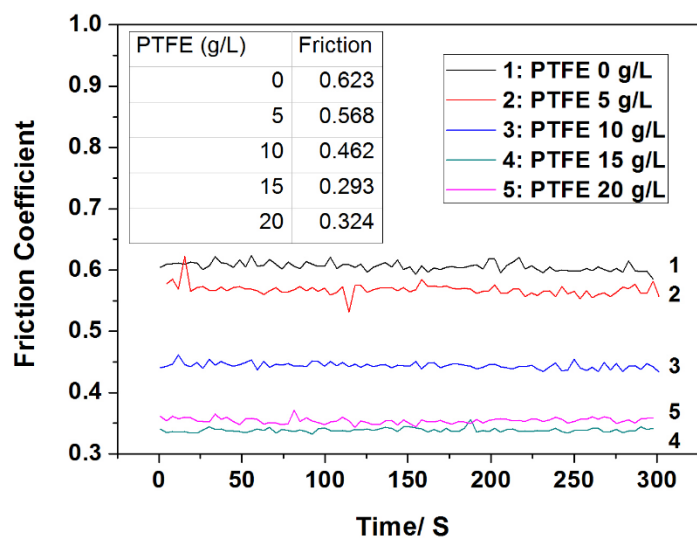


Figure 3. Effect of PTFE on friction coefficient of CoMoP/PTFE alloy films, (a) 0 g/L PTFE; (b) 5 g/L PTFE; (c) 10 g/L PTFE; (d) 15 g/L PTFE; (e) 20 g/L PTFE; The length of wear mark is 10 mm with 10 N force for 5 min.

It can be seen from Fig.3 that the friction coefficient of the CoMoP/PTFE film decrease first and then increases along with the increase of PTFE concentration in the plating solution. The alloy film prepared at the concentration of 15 g/L PTFE has the lowest friction coefficient. PTFE is a kind of polymer materials with lower friction coefficient. [23] During the sliding wear process, PTFE is easy to be destroyed to form polymer lubrication film on the friction surface which contributes directly to the great reduce of the wear rate reported by some researchers.[24-26] Many PTFE particles are evenly embedded in the CoMoP/PTFE alloy film. During the friction process, PTFE particles in the bottom layer are constantly exposed to the surface which reduces the friction coefficient. When the concentration of PTFE in the solution is greater than 15 g/L, the agglomeration effect increases the surface roughness resulting in the increase of friction coefficient.

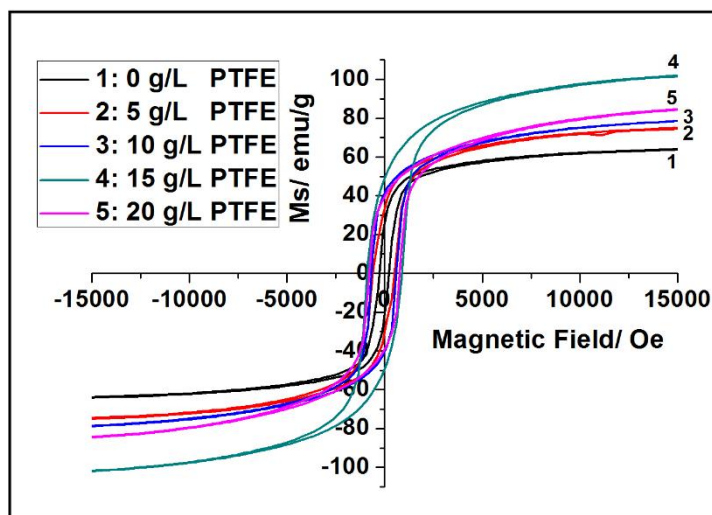


Figure 4. Effect of PTFE on magnetic performance of CoMoP/PTFE alloy films, (1) 0 g/L PTFE; (2) 5 g/L PTFE; (3) 10 g/L PTFE; (4) 15 g/L PTFE; (5) 20 g/L PTFE; Applied magnetic field is from 0 to 1.5 T; Averaging time per point is 10 s;

Magnetic hysteresis loop is used to evaluate the magnetic performance of CoMoP/PTFE alloy film based on coercivity and saturation magnetization shown in Fig.4 and Tab.2.

Table 2. Coercivity and saturation magnetization of CoMoP/PTFE

PTFE concentration/ g/L	Coercivity/ Oe	Ms/ emu/g
0	217.16	65.15
5	506.27	76.39
10	600.82	81.72
15	893.14	105.61
20	754.23	88.54

According to the Fig.4 and Tab.2, CoMoP alloy film deposited from the solution without PTFE has lower coercivity and saturation magnetization. With the increase of PTFE concentration, the coercivity and saturation magnetization of CoMoP/PTFE alloy film increase gradually. The alloy film obtained at the condition of 15 g/L PTFE possesses optimal magnetic performance with maximum coercivity and saturation magnetization. Higher concentration of PTFE in the plating solution is beneficial to increase the deposition rate resulting in the increase of cobalt content in the alloy film which attributes to the increase of saturation magnetization. Moreover, the PTFE nanoparticles codeposited with CoMo could enter the grain boundary and lattice of CoMo alloy, so as to refine the grains and improve the coercivity. However, agglomeration effect produced by excessive PTFE decreases deposition rate and cobalt content resulting in the decrease of coercivity and saturation magnetization.

3.3 Effect of PTFE on corrosion resistance and surface morphology of CoMoP/PTFE alloy films

Tafel extrapolation method is used to calculate the self corrosion potential and corrosion current of the alloy films in 3.5% sodium chloride solution shown in Fig.5 and Tab.3. It can be seen from Tab.3 that CoMoP/PTFE obtained from the bath with different PTFE concentrations possesses different self potentials and corrosion currents. PTFE is an inert polymer with very high impedance which can effectively reduce corrosion current to inhibit electrochemical corrosion process.[27-28] Therefore, with the increase of the concentration of PTFE in the plating solution, the content of PTFE in the alloy film increases, so that the corrosion current of the sample decreases sharply, which greatly improve the corrosion resistance performance of CoMoP/PTFE alloy film. The film prepared at 15 g/L PTFE has the best corrosion resistance with the lowest corrosion current density. When the PTFE concentration is higher than 15 g/L, agglomeration effect produced by excessive PTFE would decrease the deposition rate and deteriorate the film quality resulting in the decrease of corrosion resistance performance. PTFE is beneficial to improve corrosion resistance of substrate which is also investigated in some literatures. [29-30]

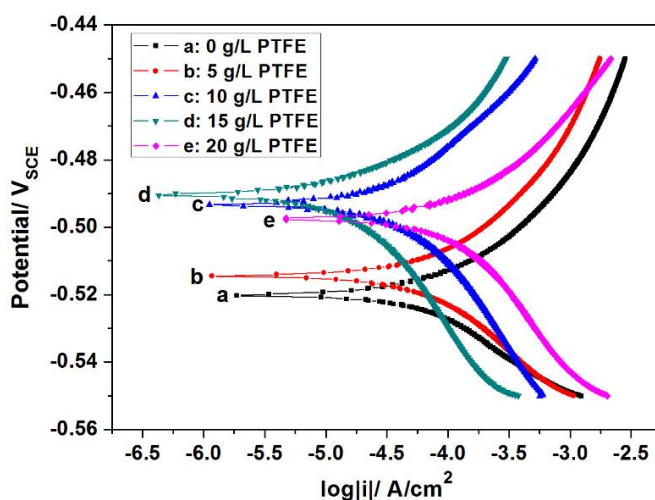


Figure 5. Effect of PTFE on polarization curves of CoMoP/PTFE alloy films in 3.5% sodium chloride , (a) 0 g/L PTFE; (b) 5 g/L PTFE; (c) 10 g/L PTFE; (d) 15 g/L PTFE; (e) 20 g/L PTFE; The scanning potential is from -0.55 V to -0.45 V at 3 mV/s scanning rate. Cathode:1 cm×1 cm CoMoP/PTFE film; Anode:3 cm×3 cm platinum sheet; Reference: saturated calomel electrode; Corrosion solution: 3.5% Sodium chloride.

Table 3. Corrosion resistance performance of CoMoP/PTFE alloy film

PTFE Concentration/ g/L	E_c/ V_{SCE}	$i_c/ \mu A/cm^2$
0	-0.520	68.4
5	-0.515	61.5
10	-0.493	30.1
15	-0.490	14.0
20	-0.497	78.2

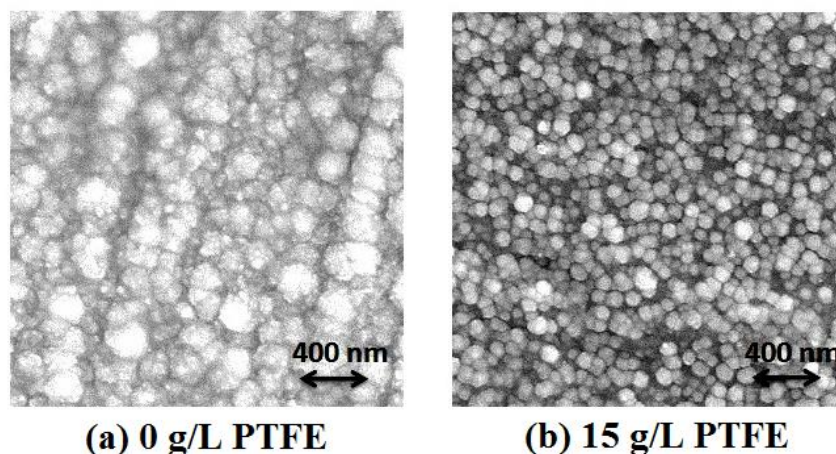


Figure 6. Effect of PTFE on surface morphology of CoMoP/PTFE alloy film, (a) 0 g/L PTFE; (b) 15 g/L PTFE; Magnification 10k;

According to the analysis of previous sections, CoMoP/PTFE alloy film prepared under the condition of 15 g/L PTFE has the best corrosion resistance and magnetic performance. Therefore, scanning electron microscope is used to observe the surface morphology of this optimal film, as shown in Fig.6. The film without PTFE shows nodular structures composed of uneven particles. However, the CoMoP/PTFE obtained from 15 g/L PTFE solution shows smaller and denser nodular structures. During the codeposition process, nano PTFE particle can enter the grain boundary and lattice of CoMo to reduce the grain size resulting in denser surface morphology.

4. CONCLUSION

CoMoP/PTFE alloy film was prepared by electrodeposition technology. Effect of PTFE concentration on deposition rate, thickness, magnetic performance and corrosion resistance of CoMoP/PTFE was investigated. The results show that PTFE is beneficial to increase deposition rate, decrease friction coefficient, increase corrosion resistance and magnetic performance of CoMoP/PTFE alloy film. However, when the concentration of PTFE is greater than 15 g/L, excessive PTFE tends to agglomerate in the bath resulting in the decrease of deposition rate and thickness. The film prepared under the condition of 15 g/L PTFE has uniform and compact structure with best corrosion resistance and magnetic performance.

ACKNOWLEDGEMENTS

This work was supported by Youth Innovation Team of Shaanxi Universities (2019-73) and Project of Xi'an Aeronautical Polytechnic Institute (20XHZZK-12).

References

1. Y. M. Mu, P. Li, Y. M. Wen, S. M. Yu, Y. Wang and L. X. Bian, *J. Magn. Magn. Mater.*, 533 (2021) 168025.
2. B. S. Ram, A. K. Paul and S. V. Kulkarni, *J. Magn. Magn. Mater.*, 537 (2021) 168210.
3. D. G. Gonzalez and M. Hossain, *Extreme Mech. Lett.*, 48 (2021) 101382.
4. G. Y. Wei, H. L. Ge, X. Zhu and Q. Wu, *Appl. Surf. Sci.*, 253 (2007) 7461.
5. T. K. Tsai, S. S. Wu, C. S. Hsu and J. S. Fang, *Thin Solid Films*, 519 (2011) 4958.
6. Z. A. Hamid, A. A. Aal, A. Shaaban and H. B. Hassan, *Surf. Coat. Tech.*, 203 (2009) 3692.
7. V. V. Kuznetsov, Y. Gamburg, V. V. Zhulikov and V. M. Krutskikh, *Electrochim. Acta*, 354 (2020) 136610.
8. S. Thanikaikarasan, R. Kanimozhi, M. Saravannan and R. Perumal, *Mater. Today Proc.*, 46 (2021) 10248.
9. Q. S. Chen, Z. Y. Zhou, G. C. Guo and S. G. Sun, *Electrochim. Acta*, 113 (2013) 694.
10. Y. D. Yu, G. Y. Wei, L. Jiang and H. L. Ge, *Int. J. Electrochem. Sci.*, 15 (2020) 1108.
11. L. Gang, Y. D. Yu, H. L. Ge and G. Y. Wei, *Surf. Rev. Lett.*, 25 (2018) 1850037.
12. C. J. Pan, H. Y. An, T. Harumoto, Z. J. Zhang and Y. Nakamura, *J. Magn. Magn. Mater.*, 484 (2019) 320.
13. Y. Zhou, Z. P. Sun, Y. Yu, L. Li, J. L. Song and F. Q. Xie, *Tribol. Int.*, 159 (2021) 106933.
14. P. Jin, C. F. Sun, Z. H. Zhang, C. Y. Zhou and T. Williams, *Surf. Coat. Tech.*, 392 (2020) 125738.
15. S. Mahdavi, A. A. Alamdari and M. Z. Meibodi, *Ceram. Int.*, 46 (2020) 5351.
16. Z. Liang, F. Pyczak, A. Stark, Z. Y. Rao, S. Neumeier and M. Goken, *Corros. Sci.*, 189 (2021) 109594.
17. Z. Q. Zhai, H. Abe, Y. Miyahara and Y. Watanabe, *Corros. Sci.*, 92 (2015) 32.
18. X. K. Zhao, W. Cai and L. C. Zhao, *Surf. Coat. Tech.*, 155 (2002) 236.
19. E. Gomez, E. Pellicer and E. Valles, *Surf. Coat. Tech.*, 197 (2005) 238.
20. J. H. Kim, S. Yonezawa and M. Takashima, *Int. J. Hydrogen Energy*, 36 (2011) 1720.
21. J. H. Kim, S. Yonezawa and M. Takashima, *Appl. Surf. Sci.*, 279 (2013) 329.
22. Q. Zhao, Y. Liu, H. M. Steinhausen and G. Liu, *Surf. Coat. Tech.*, 155 (2002) 279.
23. S. Sangeetha, G. P. Kalaigan and J. T. Anthuvan, *Appl. Surf. Sci.*, 359 (2015) 412.
24. R. Kumar, B. Malaval, M. Antonov and G. Zhao, *Tribol. Int.*, 147 (2020) 106282.
25. A. K. Bandaru, P. M. Weaver and R. M. Higgins, *Polym. Test.*, 103 (2021) 107369.
26. Z. B. Lin, B. Z. Gao, X. J. Li and K. F. Yu, *Tribol. Int.*, 139 (2019) 12.
27. R. Balaji, M. Pushpavanam, K. Y. Kumar and K. Subramanian, *Surf. Coat. Tech.*, 201 (2006) 3205.
28. R. D. Xu, Z. C. Guo and J. Y. Pan, *T. Nonferr. Metal Soc.*, 16 (2006) 666.
29. S. Wang, Y. Wang, Y. C. Zou, Y. F. Wu, G. L. Chen, J. Hu and O. Yang, *Chem. Eng. J.*, 402 (2020) 126116.
30. Y. Wan, Y. Yu, L. Cao, M. Zhang, J. Gao and C. Qi, *Surf. Coat. Tech.*, 307 (2016) 316.