

Effect of Trimethylamine Borane (TMAB) on the Corrosion Resistance and Mechanical Properties of Nickel-Based Composite Coatings

Hung-Hua Sheu^{2,4,*}, Qian-You Wang², Pao-Chang Huang^{3,4}, An-Yu Cheng¹, Yih-Ming Liu^{2,4}, Kung-Hsu Hou^{3,4}, Ming-Der Ger^{2,4,*}

¹ Graduate School of National Defense Science, Chung Cheng Institute of Technology, National Defense University, Taoyuan City, Taiwan

² Department of Chemical and Materials Engineering, Chung Cheng Institute of Technology, National Defense University, Taoyuan City, Taiwan

³ Department of Power Vehicle and Systems Engineering, Chung Cheng Institute of Technology, National Defense University, Taoyuan City, Taiwan

⁴ System Engineering and Technology Program, National Chiao Tung University, Hsin-Chu, Taiwan

*E-mail: shhccit@gmail.com, mingderger@gmail.com

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In this study, B₄C particles are added into “Ni bath” and “Ni-B bath” (added TMAB) to electrodeposited Ni/B₄C and Ni-B/B₄C composite coating, respectively. The purpose of this study is to understand the effects of adding TMAB to the nickel plating solution on the corrosion resistance and wear resistance of the Ni/ B₄C and Ni-B/ B₄C composite coating. The SEM images shows a looser structure occurred at Ni-B/B₄C composite coating. The i_{corr} value of Ni/B₄C and Ni-B/B₄C composite coating deposited on low carbon steel is 6.04×10^{-6} A/cm² and 1.06×10^{-4} A/cm², respectively. The reason of poor corrosion resistance of Ni-B/B₄C composite coating can be attributed to the addition of TMAB into Ni bath will change the Zeta potential of B₄C particles from 1.77 mV to -2.26 mV, and caused some reduced metal ions will preferentially deposited on the surface of particles when particles have a negative surface charge condition, the particles coated with metal ions on the surface will gather together and block the deposition of reduced metal ions on the cathode surface, finally formed a looser structure in Ni-B/B₄C composite coating. The adhesion strength of Ni-B/B₄C composite coating is approximately at 2.5 N, the adhesion strength of Ni/B₄C composite coating is approximately at 7.6 N, it indicates the looser microstructure will decrease the adhesion strength of composite Ni-B/B₄C coating.

Keywords: Ni/B₄C composite coating, Ni-B/B₄C composite coating, corrosion resistance, Zeta potential

1. INTRODUCTION

In recent years, nickel-based coatings have been widely used in the industry. Because of its excellent corrosion resistance, these nickel-based coatings include Ni, Ni-P, Ni-W, Ni-B, etc. [1-7].

Among them, the Ni-B alloy coating has a high hardness of about 900 Hv, so it is suitable for wear resistance applications [6]. In general, the preparation methods of the Ni-B coating can be divided into electroless process [8-10] and electroplating [11,12]. The former is a commonly used process for preparing Ni-B coatings, but its disadvantage is that the coating thickness has its limit (not too thick), so the wear resistance cannot be maintained for too long, the latter method for preparing Ni-B coatings is seldom studied in depth, but its advantage is that coatings with a larger thickness can be prepared. The above two methods of preparing Ni-B alloy coatings, the boron source of nickel electroplating solution come from dimethylamine borane (DMAB) [13-15] or trimethylamine borane (TMAB) [16-18], dimethylamine borane will decompose at higher temperature ($>75^{\circ}\text{C}$) and the electroplating solution is not easy to maintain, comparatively the electroplating solution containing trimethylamine borane is stable. However, the Ni-B alloy coating will accumulate excessive internal stress during the electroplating process, causing cracks in the coating and reducing corrosion resistance [14,17]. In the past research, it was pointed out that in the electroplating process, hard particles are added to the plating solution and incorporated into the alloy coatings. The formed coating is called composite coating. This composite coating can effectively reduce the internal stress of the alloy coatings and at the same time can improve the mechanical properties of the coating and increase the wear resistance. It has been successfully applied to trivalent chromium-carbon alloy coating [19-21], Ni-P alloy coating [22], Ni-W alloy coating [23,24]. In the part of hard particles, boron carbide is the ceramics whose hardness is second only to diamond. Its Mohs hardness is as high as 9.5, and its density is low (2.5 g/cm^3). Its application in the preparation of composite coating will effectively improve the wear resistance of the coating.

Therefore, in this study, boron carbide particles will be added to the nickel plating solution (divided into two conditions with added TMAB and without added TMAB). The effects of adding TMAB to the nickel plating solution on the corrosion resistance and wear resistance of the two composite coatings of Ni/B₄C and Ni-B/B₄C are discussed.

2. EXPERIMENTAL

The Ni/B₄C and Ni-B/B₄C composite coating were electrodeposited on low carbon steel substrates with a dimension of $30 \times 20 \times 2\text{ mm}$, respectively. The Ni/B₄C and Ni-B/B₄C composite coating are produced in a typical sulfamate bath of following composition: 400 g/L nickel sulfamate ($\text{Ni}(\text{NH}_2\text{SO}_3)$), 40 g/L boric acid (H_3BO_3), 10 g/L nickel chloride ($\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$), TMAB (with added 4 g/L TMAB and without added TMAB) and 2 g/L of B₄C powder. The composition of electroplating solution and the electroplating operating parameters are listed in Table 1. The average particle size of B₄C used in this study is approximately at 1.8 μm (purity 97.0 %, made by our research team).

The surface microstructure and cross sections of the coating were observed by scanning electron microscopy (SEM, Jeol model JSM-6500). The average size of the embedded particles was also determined by SEM. Vickers micro-hardness tester (TECH FM-100e) was used to measure the hardness and the mean value for the hardness is calculated after 10 tests, loading with 25 g for 15 seconds. The potentiodynamic polarization of Ni/B₄C and Ni-B/B₄C composite coating were analyzed by a standard

three-electrode cell system using an Autolab-PGSTAT30 potentiostat/galvanostat controlled by a GPES (General Purpose Electrochemical system) software and stabilized at open circuit potential (OCP) before test. The potentiodynamic polarization analysis were conducted in 3.5 wt.% NaCl solution at room temperature. The potential was ramped from -0.4 V and 0.6 V with a scanning rate of 0.45 mV s^{-1} . The Zeta potential of B_4C particles added into the “Ni bath” and “Ni-B bath” (added TMAB) are carried out by an ELSZ-2000ZS analytical Instruments. The adhesion property of Ni/ B_4C and Ni-B/ B_4C composite coating electrodeposited on low carbon steel substrates were carried out with a scratch tester (Micro Scratch Tester (MST³), Aton Paar GmbH, Germany). The load was from 0 N to 20 N, and the load was gradually applied to Ni/ B_4C and Ni-B/ B_4C composite coating to measure the critical load that the Ni/ B_4C and Ni-B/ B_4C composite coating.

Table 1. Plating bath composition and electroplating operating parameters

Composition and operating conditions			
	Ni/ B_4C composite coating	Ni-B/ B_4C composite coating	
Nickel sulfamate	400 g/L	400 g/L	
Boric acid	40 g/L	40 g/L	
Nickel chloride	10 g/L	10 g/L	
TMAB	none	4 g/L	
B_4C particles (1.8 μm)	2 g/L	2 g/L	
Temperature	55°C	55°C	
Stirring speed	400 rpm	400 rpm	
Current density	10 A/dm^2	10 A/dm^2	
pH	4	4	
Electroplating time	40 min	40 min	

3. RESULTS AND DISCUSSION

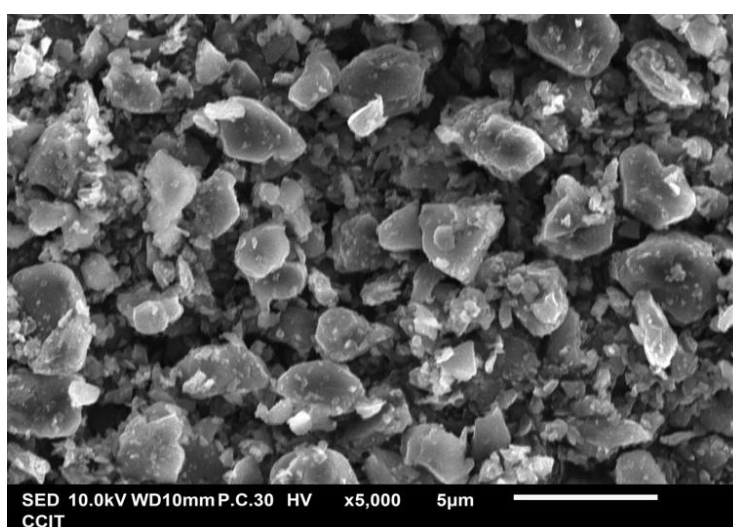


Figure 1. The SEM image of B_4C powders.

Fig. 1 shows the B₄C powders SEM image that made by our research team using chemical pyrolysis and calcined process. The shape of the boron carbide powder particles is close to spherical, and there is no obvious sharp shape. The average particle size of B₄C powders is approximately at 1.8 μm .

Fig. 2 shows the surface morphology SEM image of Ni/B₄C composite coating and Ni-B/B₄C composite coating at the same electrodeposited parameters. In Ni/B₄C composite coating, the surface morphology presents a typical smooth surface of nickel-based coating (Fig. 2(a)). On the contrary, the surface morphology of Ni-B/B₄C composite coating presents nodules structure and caves, the microstructure is very different from that of Ni/B₄C composite coating (Fig. 2(b)).

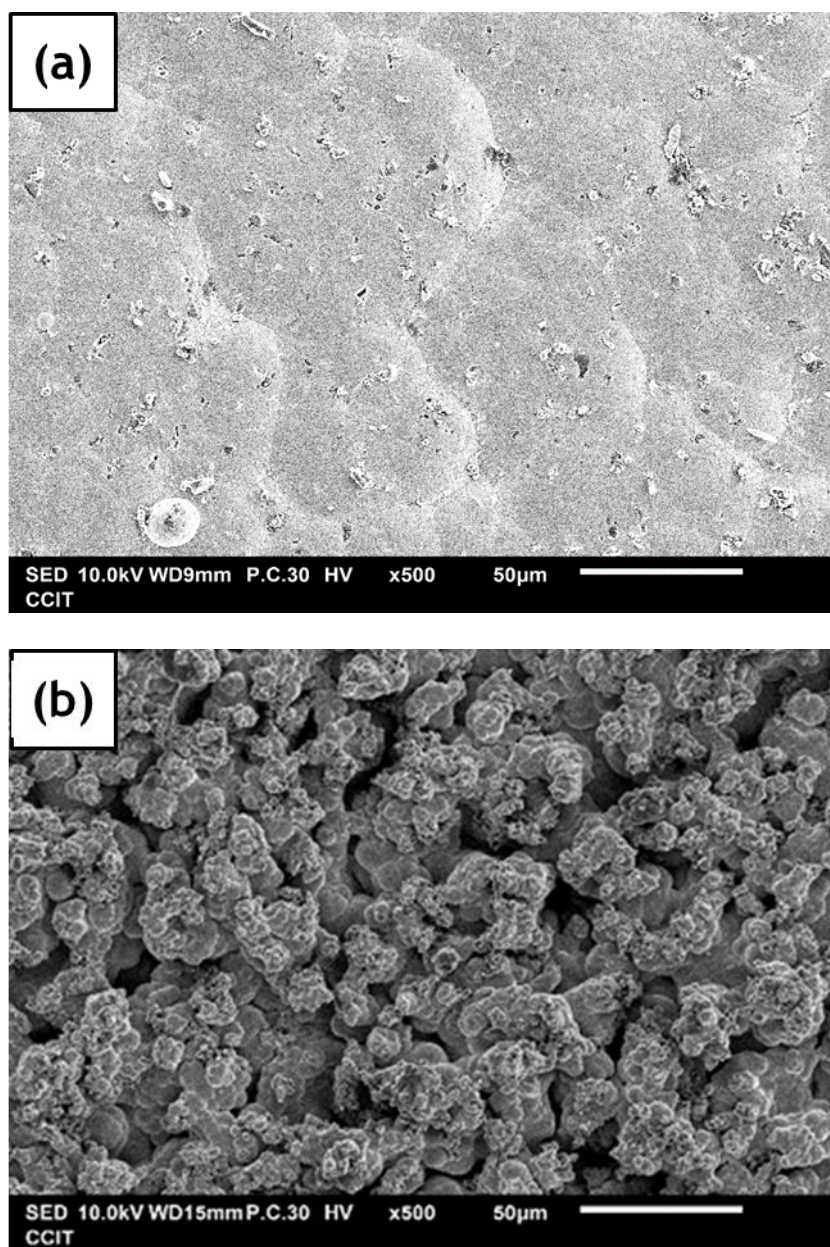


Figure 2. The SEM morphology image of Ni/B₄C composite coating (a) and Ni-B/B₄C composite coating (b) that carried out with the electrodeposited at current density 10 A/dm² for 10 mins.

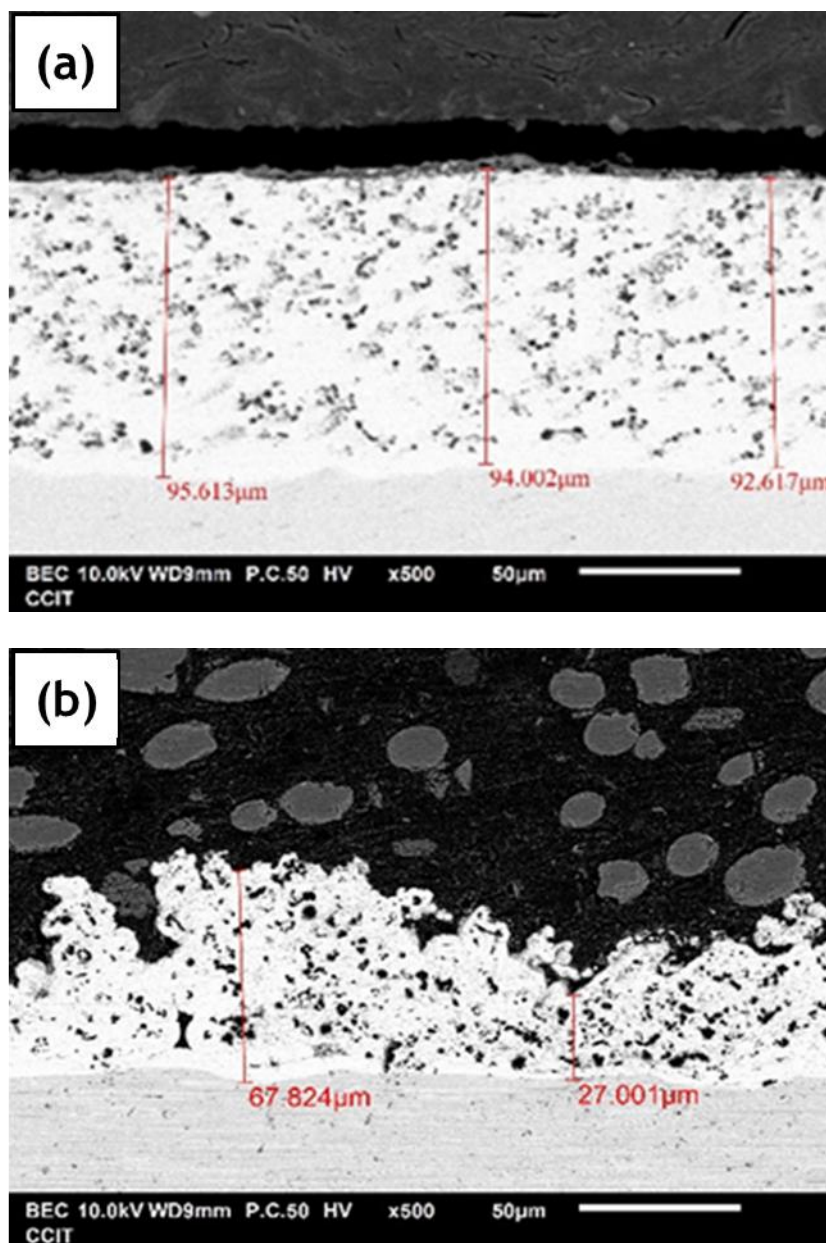


Figure 3. The SEM cross-sectional image of Ni/B₄C composite coating (a) and Ni-B/B₄C composite coating (b) that carried out with the electrodeposited at current density 10 A/dm² for 10 mins.

Fig. 3 shows the cross-sectional SEM image of Ni/B₄C composite coating and Ni-B/B₄C composite coating at the same electrodeposited parameters. Fig. 3(a) presents the cross-sectional image of Ni/B₄C composite coating electrodeposited from the plating bath without adding TMAB, the thickness of Ni/B₄C composite coating is uniform, the average thickness of Ni/B₄C composite coating is about 93.7 μm for electrodeposited 40 min. At the same electrodeposited parameters, the Ni-B/B₄C composite coating electrodeposited from the bath added 4 g/L TMAB, the cross-sectional of coating is very rough and has a loosely structure, the biggest thickness is 67.8 μm the smallest thickness is 27 μm (Fig. 3(b)).

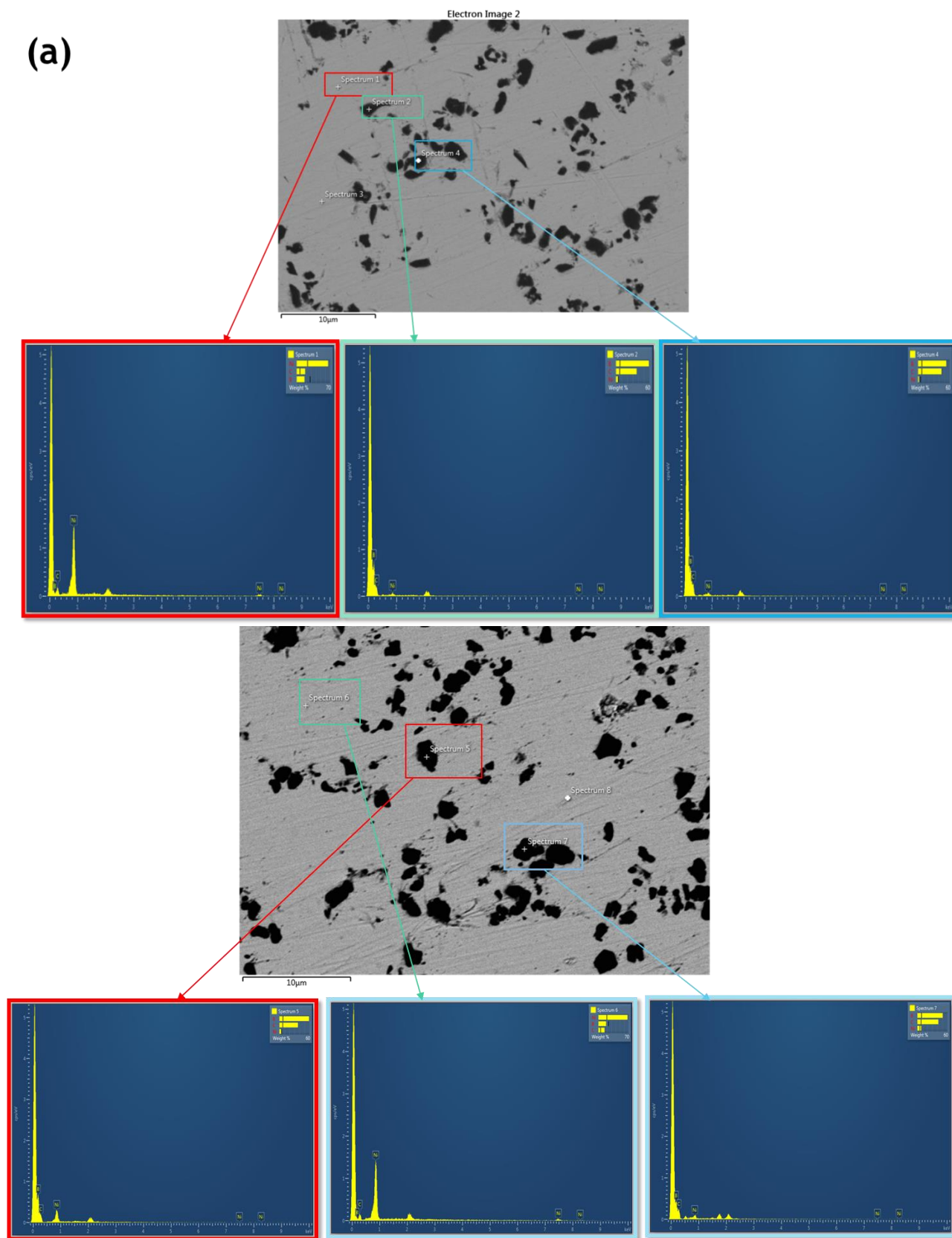


Figure 4. The EDS analysis of Ni/B₄C composite coating (a) and Ni-B/B₄C composite coating (b) that carried out with the electrodeposited at current density 10 A/dm² for 10 mins.

In order to confirm whether B₄C is deposited in the Ni/B₄C composite coating and Ni-B/B₄C composite coating, the chemical composite is analyzed by EDS and shows in Fig. 4. Fig. 4(a) shows the EDS analysis of Ni/B₄C composite coating, the red square indicates the nickel matrix, green and blue squares indicate the B₄C particles indeed co-deposited in coating. The same way to analyze the chemical composition of Ni-B/B₄C composite coating, in Fig. 4(b), the green square indicates the nickel matrix, red and blue squares also indicate the B₄C particles indeed co-deposited in coating.

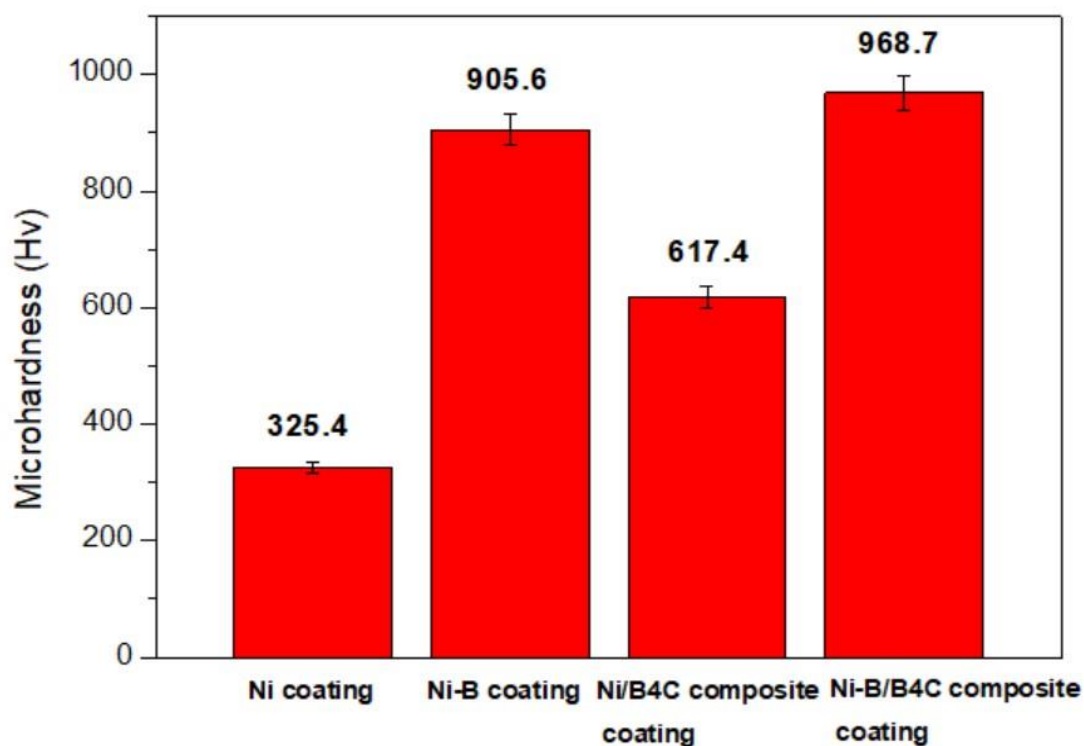
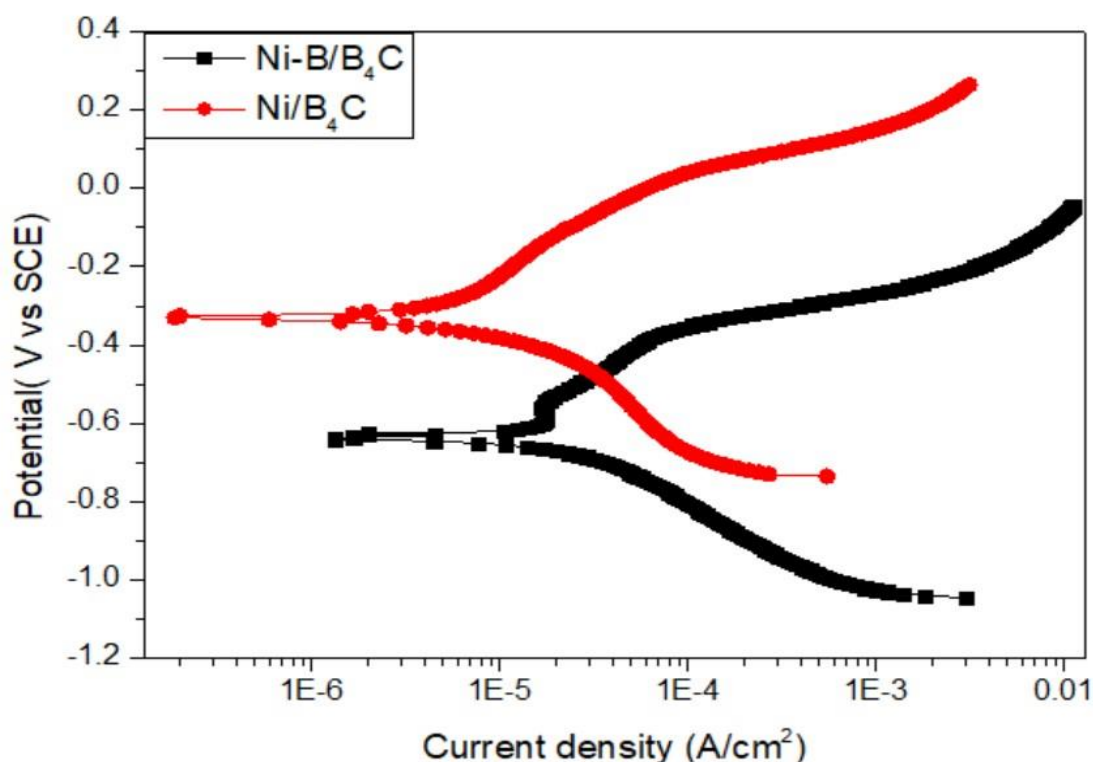


Figure 5. The micro-hardness of Ni coating, Ni-B coating, Ni/B₄C composite coating and Ni-B/B₄C composite coating that carried out with the electrodeposited at current density 10 A/dm² for 10 mins.

Fig. 5 shows the micro-hardness of Ni coating, Ni-B coating, Ni/B₄C composite coating and Ni-B/B₄C composite coating in this study, the micro-hardness is 325.4, 905.6, 617.4 and 968.7 Hv, respectively. The micro-hardness of Ni-B coating is agreement with the past studies that in the range from 750 Hv to 1100 Hv [6,25,26]. The hardness of Ni-B alloy coating is bigger than that of pure Ni coating about three times, can be attributed to an effect of solid solution strength mechanism of the boron atoms [6]. In this work, the hardness of Ni coating increase from 325.4 Hv to 617.4 Hv after added B₄C particles, this can be attributed to an effect of dispersion strength mechanism [19,20]. The hardness value of Ni/B₄C in this study is 617.4 Hv and is agreement with previous literature which their hardness is approximately at 550 Hv [27]. In Ni-B coating and Ni-B/B₄C composite coating, the hardness of Ni-B coating increase from 905.6 Hv to 968.7 Hv after added B₄C particles. Therefore, added the ceramics particles into metal or alloy coating can improve the mechanical properties of the coating, and this phenomenon has also been confirmed in the past literatures [19-24].

Table 2. Corrosion resistance of Ni/B₄C composite coating and Ni-B/B₄C composite coating analyzed from 3.5 wt.% NaCl solution.

Sample code	I_{corr} (A/cm ²)	E_{corr} (V vs. SEC)
Ni/B ₄ C composite coating	6.04×10^{-6}	-0.332
Ni-B/B ₄ C composite coating	1.06×10^{-4}	-0.645

**Figure 6.** Potentiodynamic curves of Ni/B₄C composite coating and Ni-B/B₄C composite coating electrodeposited on low carbon steel substrates that carried out with the electrodeposited at current density 10 A/dm² for 10 mins, and analyzed from 3.5 wt.% NaCl solution.

Polarization curves of Ni/B₄C composite coating and Ni-B/B₄C composite coating electrodeposited on low carbon steel substrates are shown in Fig. 6 and Table 2. The i_{corr} of Ni/B₄C composite coating and Ni-B/B₄C composite coating is approximately at 6.04×10^{-6} A/cm² and 1.06×10^{-4} A/cm², respectively. The poor corrosion resistance of Ni-B/B₄C composite coating should be caused by the looser structure such as microporous in the coating, Corrosion factors can corrode the substrate through these defects (see Fig. 3(b)). In the Nyquist diagram, the larger the diameter of the semicircular curve of the measured test piece, the higher the resistance value of the test piece, which means the better corrosion resistance of the sample [28]. The Nyquist plots also present the Ni/B₄C composite coating has higher R_{ct} ($83500 \Omega \cdot \text{cm}^2$) than that of Ni-B/B₄C composite coating ($31500 \Omega \cdot \text{cm}^2$). This also indicates that the corrosion resistance of Ni/B₄C composite coating is better than that of Ni-B/B₄C composite coating (Fig. 7).

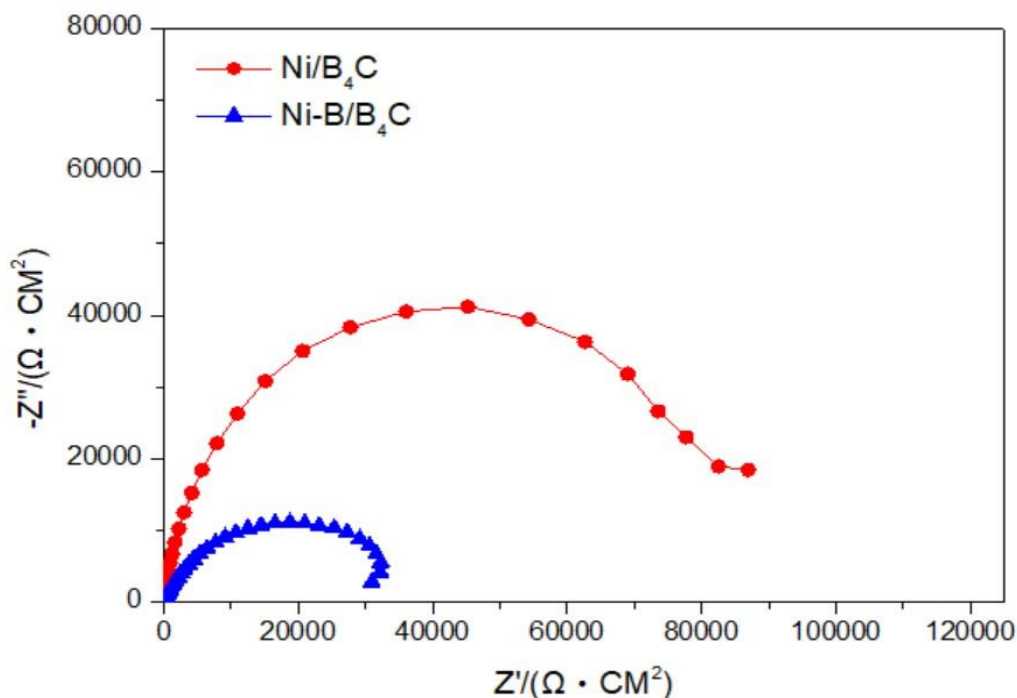


Figure 7. Nyquist diagrams of Ni/B₄C composite coating and Ni-B/B₄C composite coating electrodeposited on low carbon steel substrates that carried out with the electrodeposited at current density 10 A/dm² for 10 mins, and analyzed from 3.5 wt.% NaCl solution..

Medeliene [29] study the influence of B₄C and SiC additions on corrosion property of Ni coating and indicted that the corrosion resistance of Ni/B₄C coating is poor than that of Ni/SiC (the SiC particle is non-conductive) due to the conductive B₄C the activity of the surface increase and its stability decrease. In this study, the condition of B₄C particles incorporated into Ni matrix (Fig. 3(a)) is significantly better than that of Ni-B matrix (Fig. 3(b)). Therefore, the formation of looser structure of Ni-B/B₄C composite coating should not cause by the conductive of B₄C particles. In order to understand the surface Zeta potential of B₄C particles in the “Ni bath” and “Ni-B bath” (added TMAB), is carried out with a Zeta potential analysis, and the analyzed result is shown in Fig. 8. The Zeta potential of the surface of B₄C particles immersed in “Ni bath” is approximately at 1.77 mV, the Zeta potential of the surface of B₄C particles immersed in “Ni-B bath” (added TMAB) is approximately at -2.26 mV. The result indicates that the reason why boron carbide particles are not easily co-incorporated on Ni-B coating is not due to the conductivity of the boron carbide particles.

The particles are easily co-deposited on the cathode surface with the reduced metal ions when particles have a positive surface charge condition and to form a composite coating. On the contrary, some reduced metal ions will preferentially deposited on the surface of particles when particles have a negative surface charge condition, the particles coated with metal ions on the surface will gather together and block the deposition of reduced metal ions on the cathode surface. Thus, a looser structure formed during the electrodeposited process (Fig. 3(b)), this looser structure also will significantly decrease the corrosion resistance of the composite coating (Fig. 6). The calculated critical load of Ni/B₄C composite coating and Ni-B/B₄C composite coating deposited on substrates are shown in Fig. 9 and Table 3.

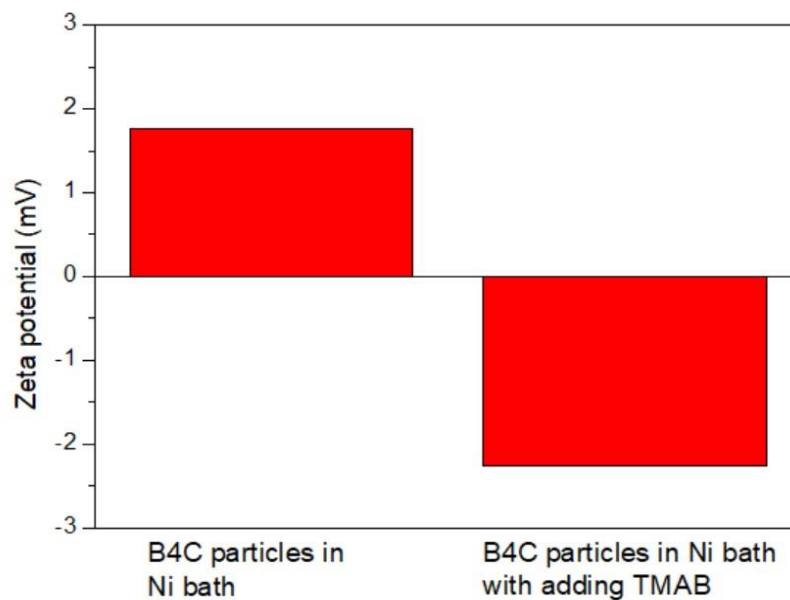


Figure 8. The Zeta potential of B₄C particles in the Ni bath and the Ni bath with adding TMAB.

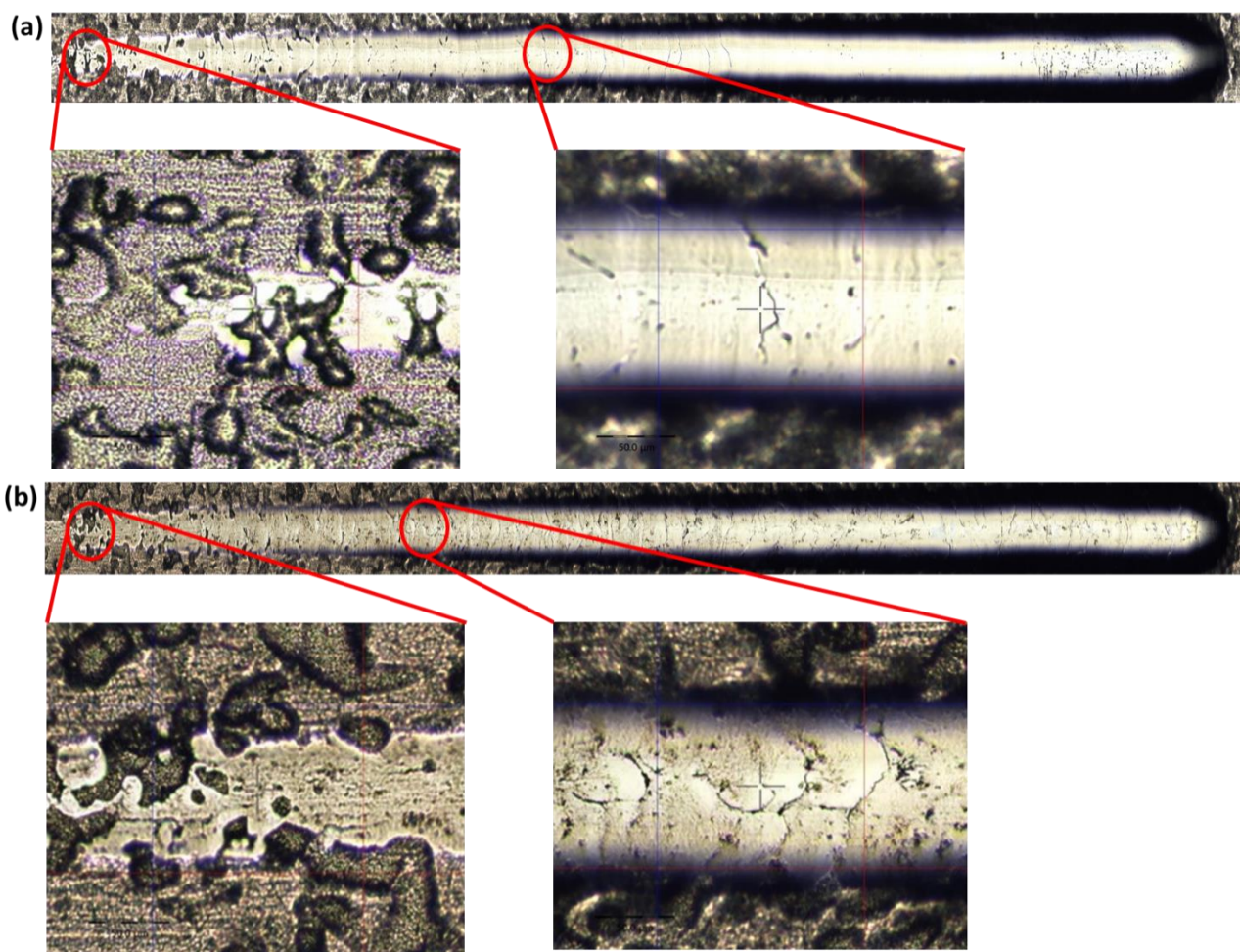


Figure 9. The scratch test images of Ni/B₄C composite coating and Ni-B/B₄C composite coating deposited on low carbon steel substrates that carried out with the electrodeposited at current density 10 A/dm² for 10 mins.

Table 3. The analysis of critical load of Ni/B₄C composite coating and Ni-B/B₄C composite coatings deposited on low carbon steel substrates that carried out with the electrodeposited at current density 10 A/dm² for 10 mins.

Sample code	L _{C1}	L _{C2}	critical load (load of L _{C2})
Ni/B ₄ C composite coating	0 mm	2.53 mm	7.6 N
Ni-B/B ₄ C composite coating	0 mm	1.6 mm	2.5 N

L_{C1} indicates the position of indenter just applied load to the surface of the coating in the scratch test, L_{C2} indicates that as the indenter gradually increases the load, the position where the coating begins to crack. The Ni/B₄C composite coating is damaged at 7.6 N, L_{C2} occurred at 2.53 mm. The Ni-B/B₄C composite coating is damaged at 2.5 N, L_{C2} occurred at 1.6 mm. The analysis of critical load presents Ni/B₄C composite coating has better adhesion strength than that of Ni-B/B₄C composite coating. This also confirms that the loose structure is not conducive to the adhesion of the composite coating.

4. CONCLUSIONS

The effect of adding TMAB into Ni solution bath on the corrosion behavior of electrodeposited Ni/B₄C composite coating and Ni-B/B₄C composite coating are studied in this study. The i_{corr} values of Ni/B₄C composite coating and Ni-B/B₄C composite coating deposited on low carbon steel is 6.04×10^{-6} A/cm² and 1.06×10^{-4} A/cm², respectively. The SEM images show the looser structure such as micro-caves formed in Ni-B/B₄C composite coating, these micro-caves will decrease the corrosion resistance of coating. The Nyquist plots also present the Ni/B₄C composite coating has higher R_{ct} ($83500 \Omega \cdot \text{cm}^2$) than that of Ni-B/B₄C composite coating ($31500 \Omega \cdot \text{cm}^2$). This also indicates that the corrosion resistance of Ni/B₄C composite coating is better than that of Ni-B/B₄C composite coating. This phenomenon is caused by the addition of TMAB into Ni electroplating solution change the Zeta potential of B₄C particles from 1.77 mV to -2.26 mV, and caused some reduced metal ions will preferentially deposited on the surface of particles when particles have a negative surface charge condition, the particles coated with metal ions on the surface will gather together and block the deposition of reduced metal ions on the cathode surface, finally formed a looser structure in Ni-B/B₄C composite coating. The addition of TMAB in Ni electroplating solution also caused a poor adhesion strength of Ni-B/B₄C composite coating.

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References

1. D.G.A. Diaz, A. B. Pingarrón, J.J.O. Florez, J.R.G. Parra, J.C.Cabello, I.A. Moncaleano, A.C. Villar, M.Á.H. Gallegos, *Mater. Lett.*, 275 (2020) 128159.

2. A.G. González-Gutiérrez, M.A. Pech-Canul, G. Chan-Rosado, P.J. Sebastian, *Fuel*, 235 (2019) 1361.
3. D. D. Shreeram, S. Li, V. Bedekar, H. Cong, G.L. Doll, *Surf. Coat. Technol.*, 325 (2017) 386.
4. P.A. Orrillo, S.B. Ribotta, L.M. Gassa, G. Benítez, R.C. Salvarezza, M.E. Vela, *Appl. Surf. Sci.*, 433 (2018) 292.
5. V. Vitry, A.F. Kanta, F. Delaunois, *Surf. Coat. Technol.*, 206 (2011) 1879.
6. H.H. Sheu, Y.C. Tzeng, J.H. Syu, *Mater. Lett.*, 238 (2019) 275.
7. A.Y. Cheng, H.H. Sheu, Y.M. Liu, K.H. Hou, P.Y. Hsieh, *Int. J. Electrochem. Sci.*, 15 (2020) 68.
8. A.F. Kanta, V. Vitry, F. Delaunois, *Mater. Lett.*, 63 (2009) 2662.
9. V. Vitry, L. Bonin, *Surf. Coat. Technol.*, 311 (2017) 164.
10. C.T. Dervos, J. Novakovic, P. Vassiliou, *Mater. Lett.*, 58 (2004) 619.
11. K.H. Lee, D. Chang, S.C. Kwon, *Electrochim. Acta* 50 (2005) 4538–4543.
12. S. Ziyuan, W. Deqing, D. Zhimin, *Appl. Surf. Sci.*, 253 (2006) 1051.
13. U. S. Waware, A.M.S. Hamouda, N. P. Wasekar, *Surf. Coat. Technol.*, 337 (2018) 335.
14. K. Krishnaveni, T.S.N. Sankara Narayanan, S.K. Seshadri, *Mater. Chem. Phys.*, 99 (2006) 300.
15. H. Ogihara, K. Udagawa, T. Saji, *Surf. Coat. Technol.*, 206 (2012) 2933.
16. E. Ünala, İ.H. Karahan, *Surf. Coat. Technol.*, 333 (2018) 125.
17. B. Li, W. Zhang, Y. Huan, J. Dong, *Surf. Coat. Technol.*, 337 (2018) 186.
18. I. Matsui, N. Omura, T. Yamamoto, Y. Takigawa, *Surf. Coat. Technol.*, 337 (2018) 411.
19. H.H. Sheu, M.H. Lin, S.Y. Jian, T.Y. Hong, K.H. Hou, M.D. Ger, *Surf. Coat. Technol.*, 350 (2018) 1036.
20. H.H. Sheu, T.Y. Hong, T.T. Lin, M.D. Ger, *Int. J. Electrochem. Sci.*, 13 (2018) 9399.
21. H.H. Sheu, C.E. Lu, K.H. Hou, M.L. Kuo, M.D. Ger, *J. Taiwan Inst. Chem. E.*, 48 (2015) 73.
22. H.H. Sheu, S.Y. Jian, M.H. Lin, C.I. Hsu, K.H. Hou, M.D. Ger, *Int. J. Electrochem. Sci.*, 12 (2017) 5464.
23. K.H. Hou, H.T. Wang, H.H. Sheu, M.D. Ger, *Appl. Surf. Sci.*, 308 (2014) 372.
24. H.T. Wang, H.H. Sheu, M.D. Ger, K.H. Hou, *Surf. Coat. Technol.*, 259 (2014) 268.
25. E. Duru, F. Dogan, M. Uysal, H. Akbulut, S. Aslan, *Surf. Interfaces*, 22 (2021) 100880.
26. Y. Liang, Y.S. Li, Q.Y. Yu, Y.X. Zhang, W.j. Zhao, Z.X. Zeng, *Surf. Coat. Technol.*, 264 (2015) 80.
27. J.B. Jiang, W.D. Liu, L. Zhang, Q.D. Zhong, Y. Wang, Q.G. Zhou, *Adv. Mat. Res.*, 399-401 (2012) 2055.
28. C. Liu, Q. Bi, H. Ziegele, A. Leyland, A. Matthews, *J. Vac. Sci. Technol.*, A 20 (2002) 772.
29. V. Medeliene, *Surf. Coat. Technol.*, 154 (2002) 104.