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Electrodeposition and Mechanical Properties of Ni-W Matrix Composite Coatings with Embedded Amorphous Boron Particles

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Hard nickel-tungsten/boron (Ni-W/B) composite coatings were designed and successfully prepared on the surface of low carbon steel by direct current electrodeposition. The effect of boron concentration in the solution on the amount of boron contents in the deposits and mechanical properties were investigated. SEM and EDS elemental mapping show a uniform dispersion of boron particles into the Ni-W matrix could be observed. ICP results reveal that high boron content (~21.7 wt.%) of composite coatings can be achieved at boron concentration of 5 g/L. High hardness of 1266 HK was obtained from the Ni-W/B composite coatings with higher boron contents. This method is much easier to obtain a high hardness of Ni-W/B coatings which is comparable to that of hard chromium plated coatings. Furthermore, the wear resistance is also enhanced for the Ni-W coatings with incorporation of boron particles.

Keywords: Composite coatings; Electrodeposition; Boron; Hardness; Wear resistance

1. INTRODUCTION

Metal matrix composite coatings containing dispersed particles usually exhibit some good properties such as dispersion hardening, self-lubricity, improved wear and corrosion resistance [1-4]. In order to enhance the properties of materials surface, coatings are usually coated onto the materials by using dry processes (e.g., chemical or physical vapour deposition methods) or wet processes (electrodeposition or electroless plating). The dry process can provide high-quality, super-hard coatings, but it needs extreme reaction conditions and precise control of gas flow. In contrast, the wet process is a simple method. For example, plating (i.e., electrodeposition), which is one of the most important techniques for fabricating nanocomposite and nanocrystal hard coatings [5-10].

The electrodeposited films show excellent functional properties and decorative applications and improve its operating properties subjected to external hazards. Recently, the developed Ni-W coatings exhibit higher hardness, higher heat resistance and also a better corrosion behaviour compared to Ni coatings [9-11]. However, the hardness of Ni-W still can't compare to the traditional chromium coating, which exhibits high hardness of ~10 GPa[10]. Incorporation of hard particles to the Ni-W nanocoatings could further enhance the hardness and wear resistance of Ni-W coating. The Ni-W/hard particles composite coatings which have been investigated and fabricated successfully include Ni-W/diamond [7, 12, 13], Ni-W/WC[14], Ni-W/Al_2O_3[15], and Ni-W/SiO_2[16]. Boron, the elemental neighbour to carbon in the periodic system of elements, which is also known to be superhard material [17, 18]. The high hardness of boron could also improve the nanostructured Ni-W coatings. However, there is no report on the effect of boron on the microstructure and mechanical properties of nanostructured Ni-W coating.

In this work, the Ni-W/B composite coatings were prepared by electrodeposition in a Ni-W plating bath containing amorphous boron particles. Afterwards, surface and cross-section morphology of those composites were observed to determine the effect of the incorporation of boron particles. The microhardness and wear performance of the composites was studied to determine the influence of boron particles. In particular, we measured the boron content in the coatings and determined the relationship between boron content and microhardness of the composite coatings. The strengthening mechanism for the coatings was also discussed according to the experimental evidences.

2. EXPERIMENTAL DETAILS

The Ni-W/B composite coatings were fabricated by a direct current electrodeposition method in a Ni-W plating bath with boron particles suspension. The Ni-W plating bath can be prepared using the following chemicals: 18 g/L $NiSO_4 \cdot 6H_2O$, 53 g/L $Na_2WO_4 \cdot 2H_2O$, 168 g/L $Na_3C_6H_5O_7 \cdot 2H_2O$, 31 g/L NH_4Cl, 18 g/L NaBr. Amorphous boron particles with concentration of 1 g/L, 3 g/L, 5 g/L, and 10 g/L were used. The received boron powder was examined by scanning electron microscopy (Fig. 1(a)). The particle size was analysed by software as shown in Fig. 1(b). The results show that the boron particles have the size ~0.03-1.27 μm, and mean size ~0.14 μm. All specimens were deposited onto low carbon steel substrates of commercial purity. The steel substrates were masked with insulated tape to leave 20×20 mm^2 of exposed area. The platinum mesh was applied as counter electrode with a spacing of approximately 5 cm between the two electrodes. The basic electrodepositing parameters were the direct current density of 0.1 A/cm^2, a depositing time of 120 min, an electrolyte stirring speed of 100 rpm, an electrolyte temperature of 75 °C, and a pH value of 8.9. All chemicals were the analytic grade reagents (CARLO). Before electrodeposition, the electrolyte with suspending the boron particles was stirred at 400 rpm for 1 h and sonicated for 30 min to prevent the particle agglomeration. Prior to each experiment, the steel plates were pre-treated in alkaline sodium hydroxide solution (60 °C), hydrochloric acid (14%) solution, and then rinsed in distilled water. The direct current was applied to the system by a rectifier (SMD-10P, Dashun, Handan, China).

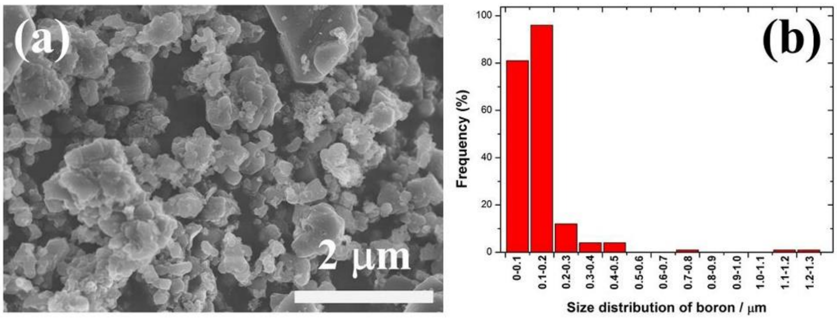

Figure 1. (a) SEM images of amorphous boron particles (b) size distribution of boron particles.

The surface morphology and the composition (Ni and W contents) were studied by scanning electron microscopy (SEM, Hitachi, S4800) and energy-dispersive spectroscopy (EDS), respectively. To determine the boron content in the deposits, the samples were measured using an inductively coupled plasma emission spectrometer (ICP-MS, Thermo Scientific). The phases of the composite coatings were analysed by X-ray diffraction (XRD) using an X'Pert Pro diffractometer (Panalytical). The surface profilometer (Gauges, Ambs, US) was carried out to measure the surface roughness. Knoop microhardness for the surface of coatings was calculated by using a microhardness tester under an indentation load of 100 gf for 15 s after seven different measurement points.

The wear performance was tested by using a CSM reciprocating-sliding tribometer. During the wear testing, the dynamic coefficient of friction was monitored by the connected computer. Si_3N_4 ball, with a load of 10 N, was set to run at 100 mm/s with reciprocation amplitude of 10 mm and without lubrication at room temperature of 20-25 ºC. Because the Si_3N_4 ball is harder than the obtained coatings, the ball can wear the coatings, and lower wear resistance will generate the larger surface area of wear track. Therefore, in this study, the wear performance is evaluated using the surface area of wear track.

3. RESULTS AND DISCUSSION

The Ni-W/B composite coatings were successfully prepared by co-deposition of boron particles with Ni-W alloy under magnetic stirring. Figure 2 shows the SEM images of the typical surface morphology of the as-deposited Ni-W and Ni-W/B composite coatings. It can be seen that all samples exhibit the columnar structure. With the boron incorporation, the columnar size becomes smaller. The Ni-W/B composite coatings (Fig. 2 (b-d)) are much more uniform, smooth, and compact surface structure compared to Ni-W coatings (Fig. 2(a)). Furthermore, the addition of boron particles in the Ni-W matrix decreases the surface roughness and alters the chemical composition. The average surface roughness (Ra) of electrodeposited Ni-W coatings is 1.58±0.1 µm, while Ra of electrodeposited Ni-W/B composite coatings is 1.26±0.07 µm, 0.93±0.04 µm, 1.13±0.08 µm, and 1.19±0.06 µm, for boron concentration in the plating bath of 1 g/L, 3 g/L, 5 g/L, and 10 g/L, respectively. The surface roughness further reveals that the addition of boron can smooth the surface. This behavior has been reported by previous researchers for Cu-Si_3N_4 composite coatings [19]. Moreover, the surface roughness increases with the increasing concentration of boron above 3 g/L, this may be caused by the boron particles cohering and forming secondary particles in the solution when the boron concentration is larger than 3 g/L. The similar result was also obtained for the composite coatings of Ni-W/MWCNT[4].

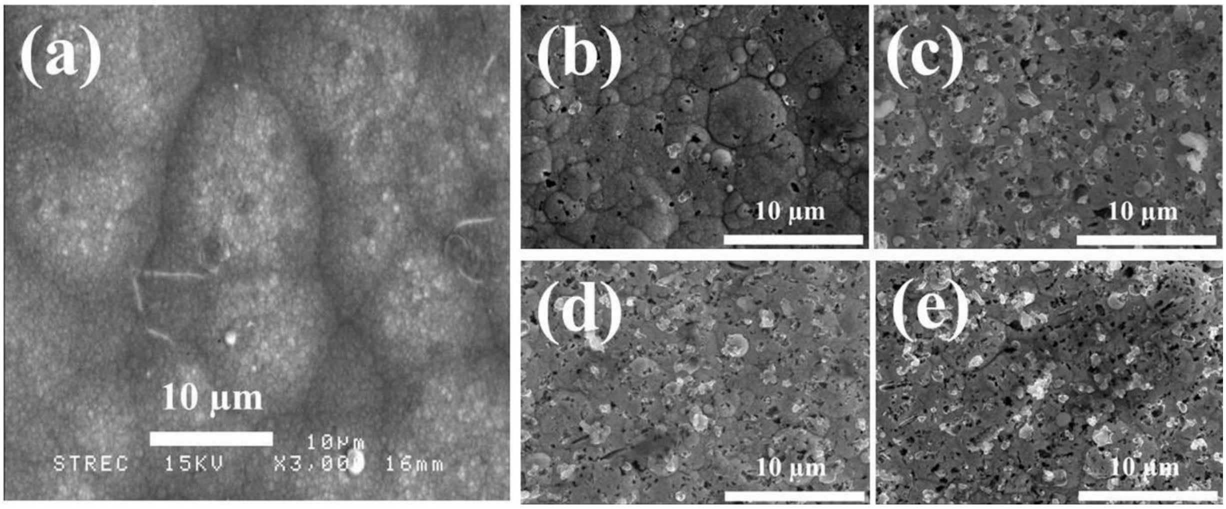

Figure 2. SEM images of Ni-W coating (a), Ni-W/B composite coatings with different boron concentration in the plating bath, (b) 1 g/L, (c) 3 g/L, (d) 5 g/L, (e) 10 g/L.

The EDS elemental mapping was also carried out to study the element distribution of as-deposited Ni-W/B composite coatings obtained with different concentration of boron in solution. Figure 3(a, b) show the Ni and W elemental mapping, respectively, for the Ni-W/B composite coatings. Figure 3(c-f) present the boron elemental mapping images of Ni-W/B composite coatings prepared with 1g/L, 3 g/L, 5 g/L, and 10 g/L, respectively. The boron EDS mapping shows that boron particles are uniformly distributed in the Ni-W alloy matrix. The boron EDS mapping also indicates that the boron content increases with concentration of boron particles in bath from 1 to 5 g/L, while above 5 g/L, the boron content slightly decreases.

The boron content in the composite coatings was further determined by ICP. Fig. 4 shows the relationship between boron concentration in solution and boron content in deposits. From the results presented in Fig. 4, it is interesting to find that the amount of embedded boron particles in the deposits increases sharply with boron concentration in the bath from 1 to 5 g/L, while above 5 g/L, the boron content slightly decreases. The maximum boron content in deposits (~21.7 wt.%) can be obtained according to the ICP results. Moreover, the cross-section morphology and the distribution of boron particles in the Ni-W matrix were also investigated.

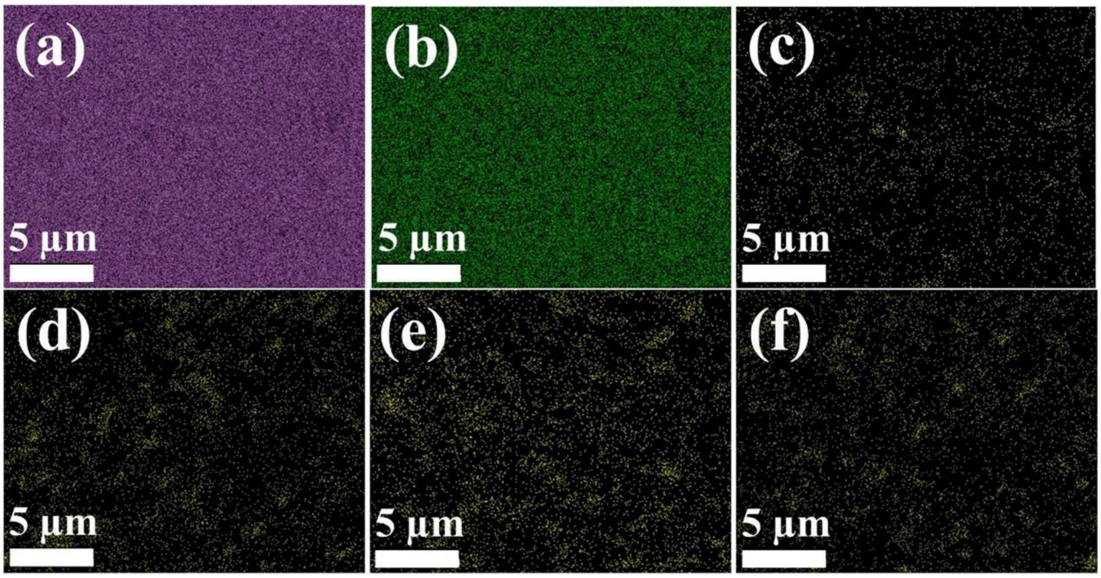

Figure 3. EDS elemental mapping images, (a) Ni, (b) W, and B in the Ni-W/B composite coatings prepared at different boron concentration in plating bath, (c) 1 g/L, (d) 3 g/L, (e) 5 g/L, (f) 10 g/L.

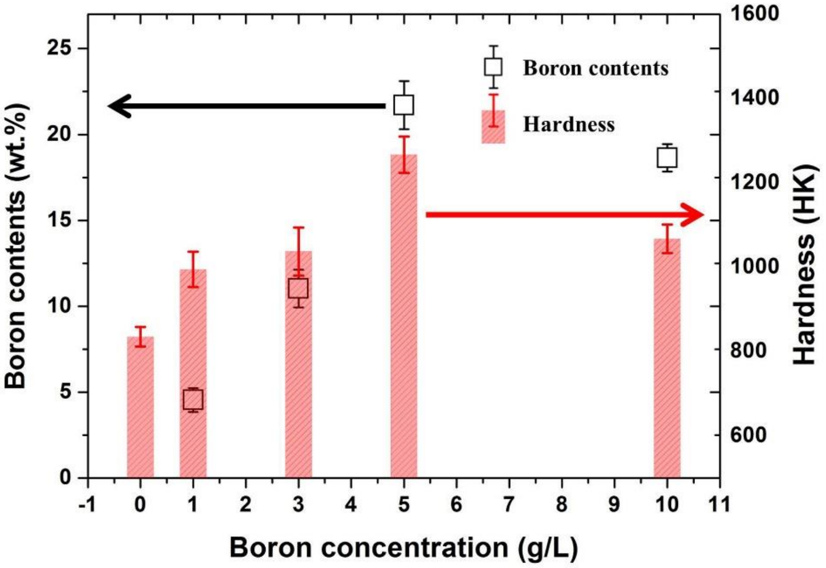

Figure 4. (a) The effect of boron concentration in the bath on boron content (left axis) and hardness of coatings (right axis).

Figure 5(a-d) show cross-sectional SEM images of the Ni-W/B composite coatings fabricated with 1 g/L, 3 g/L, 5 g/L, and 10 g/L, respectively. The thickness of Ni-W/B composite coatings was measured (~47-49 μm) from the cross-sectional SEM images, as shown in Fig. 5. It further implies that boron particles of sub-micron sizes (< 1 µm) are uniformly co-deposited into the Ni-W matrix, and many boron particles are embedded in Ni-W deposition matrix. Moreover, from the cross-sectional SEM images, the volume percentages of boron particles in coating could be estimated by image analysis software (ImageJ). The image analysis results show that the volume percentage of incorporated boron particles into Ni-W matrix is 7 vol.%, 15 vol.%, 20 vol.%, and 18 vol.%, for boron concentration in the bath of 1 g/L, 3 g/L, 5 g/L, and 10 g/L, respectively. This trend of boron content in the coatings is in good agreement with the ICP measurement and EDS elemental mapping.

In the current study, the deposited surface area is 20×20 mm^2, and the thickness of all composite coatings is ~47-49 µm (Fig. 5), then the volume of all composite coatings is almost same. Therefore, the volume percentage of deposited Ni-W matrix is 93 vol.%, 85 vol.%, 80 vol.%, and 82 vol.%, for boron concentration in the bath of 1 g/L, 3 g/L, 5 g/L, and 10 g/L, respectively. This result demonstrated that the amount of Ni-W in the coating that was deposited in the electrolyte declined as the boron concentration increased. In the Ni-W and boron particles co-electrodeposition system, there is competition between boron and metals during the co-deposition process, boron particles can be absorbed onto the surface of the cathode. The boron particles would shield the growth of crystals, resulting in decelerating the Ni-W deposition rate, yielding smaller and better grain sizes of Ni-W coating, finally forming a compact and uniform coating structure.

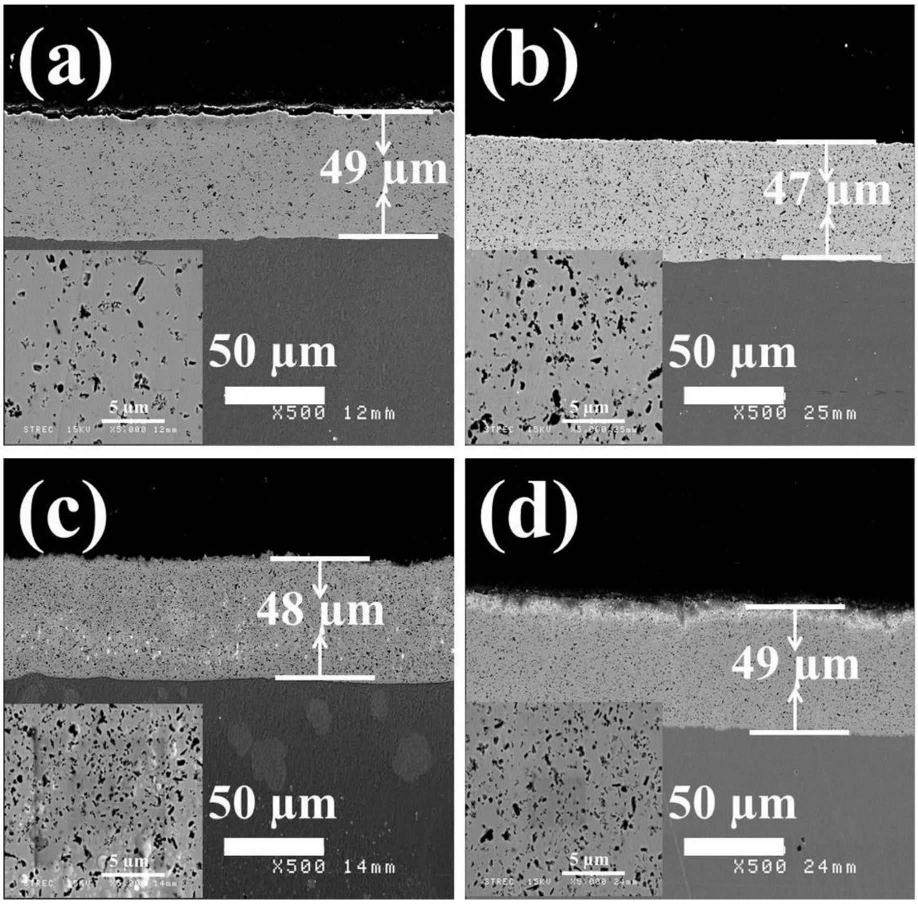

Figure 5. Cross-sectional SEM images of Ni-W/B composite coatings with different boron concentration in bath, (a) 1 g/L, (b) 3 g/L, (c) 5 g/L, (d) 10 g/L.

According to the results from EDS mapping observation, ICP measurement, and ImageJ software analysis, the boron content in the coatings increases sharply with boron concentration in the bath from 1 to 5 g/L, while above 5 g/L, the B content slightly decreases. Here, we can explain the mechanism of incorporation of boron particles in the electrodeposited Ni-W matrix by Gugliemi's model[20]. According to Guglielmi's two step adsorption model, the increase in the boron content in the deposits observed up to 5 g/L is attributed to the increase in the number of particles in the plating bath. The higher concentration can improve the adsorption rate of boron particles on the growing coatings. Thus, a higher percentage of boron particles in Ni-W matrix could be obtained according to Yeh and Wan results[20]. While the boron concentration in bath reached at 10 g/L, the boron content is lower than that of coating prepared at 5 g/L. Thus it might be due to the agglomerate of boron particles with much higher boron concentration in the plating bath. Similar results were also reported by the other researchers [13, 21-23]. At the high boron concentration of 10 g/L, some boron particles in the deposition bath might aggregate together. Therefore, the boron content might decrease at 10 g/L of boron concentration in the plating bath because their size increases due to aggregation. In the current study, the boron concentration of 5 g/L is an optimized value in the Ni-W plating bath to prepare the maximum boron content in coating.

The chemical composition was also determined by EDS. The effect of boron concentration in the plating bath on the W content in the deposits is plotted in Fig. 6. The results reveal that the W content in the coatings decreases slightly with boron concentration in the plating bath increasing. From the Fig. 6, the boron concentration in the plating bath was increased from 0 to 10 g/L, the W content in the deposits decreased from ~42 wt.% to ~38 wt.%. Hou et al. [13] also reported a similar tendency in Ni-W/diamond electrodeposition system. The boron particles in the plating bath could absorb hydrogen ions near the cathode and inhibit the reduction reaction of hydrogen ion to hydrogen. The W content in the deposits decreasing might be caused by the hydrogen ions absorbed by boron particles in the plating bath [24, 25].

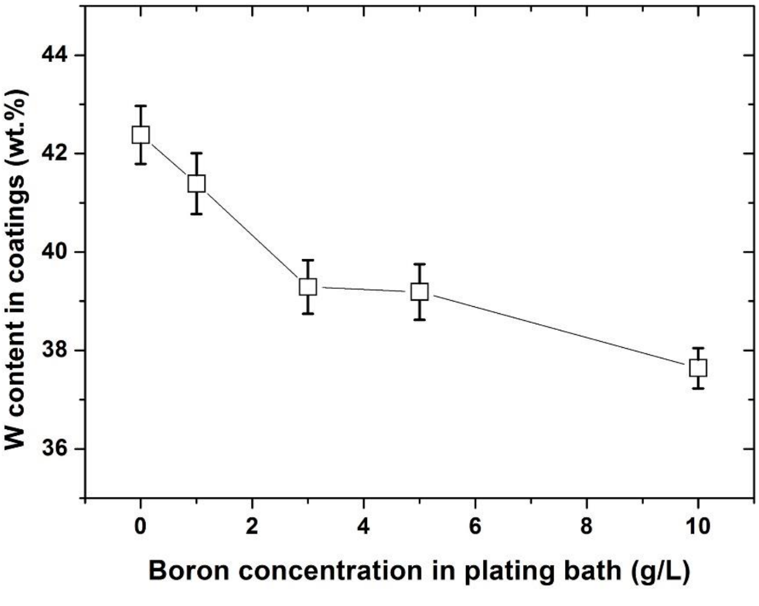

Figure 6. The dependence of W content in Ni-W and Ni-W/B coatings on the boron concentration in the plating bath.

The XRD patterns of coatings with different boron concentration in solution is shown in Fig. 7. From the XRD results, the phase for all the obtained coatings appears to be similar. Ni(W) solid solution can be identified for all the as-deposited films. The incorporation of boron particles to the Ni-W coating does not affect the coatings in terms of phase and their texture. Furthermore, the grain size of Ni-W and Ni-W/B coatings was also estimated from the width of the Ni (111) peaks. The grain size is 2.8 nm, 2.4 nm, 2.3 nm, 2.2 nm, and 2.3 nm, for 0 g/L, 1 g/L, 3 g/L, 5 g/L, and 10 g/L of boron concentration in bath, respectively.

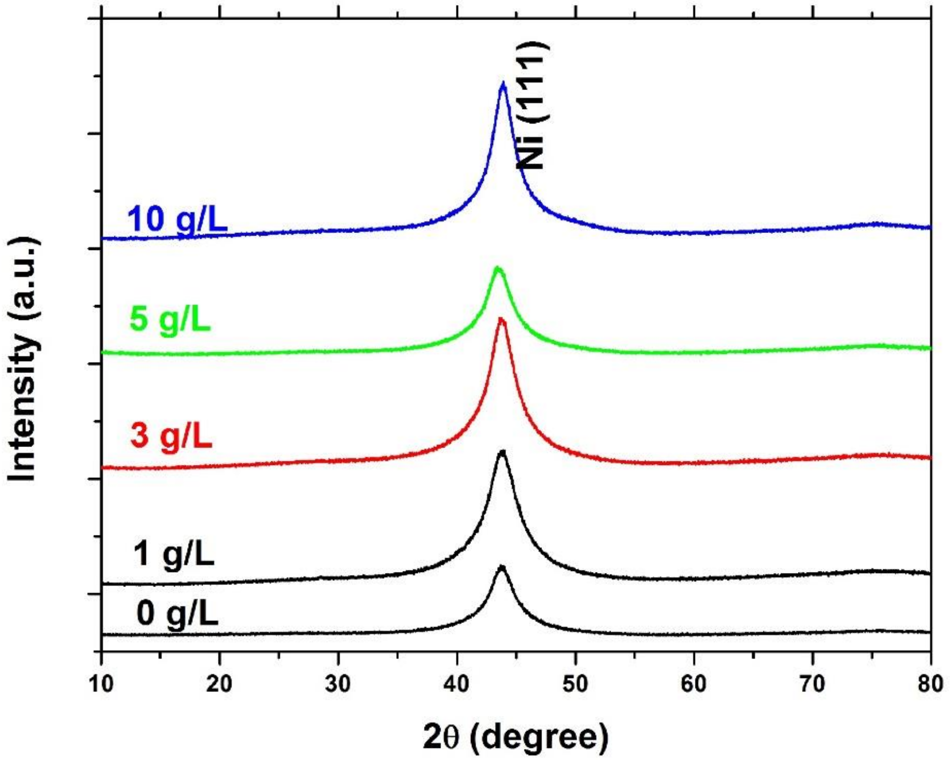

Figure 7. XRD patterns of coatings with different boron concentration in the plating bath.

The microhardness of Ni-W and Ni-W/B coatings was measured by Knoop Hardness Tester, as shown in Fig. 4. Without incorporation of boron particles, the electrodeposited Ni-W coating exhibits the hardness of 835 HK at current density of 0.1 A cm^{-2}, which is little higher than that of the reported vickers microhardness value[10]. The incorporations of boron particles of 1, 3, 5, and 10 g L^{-1}, have the hardness of 994, 1037, 1266, and 1067 Hk, respectively (Fig. 4). The hardness results indicate that the incorporation of boron in coatings can result in a marked enhancement of hardness. The hardness increases with the increase in boron concentration in the plating bath from 1 to 5 g/L, while above 5 g/L, the hardness decreases.

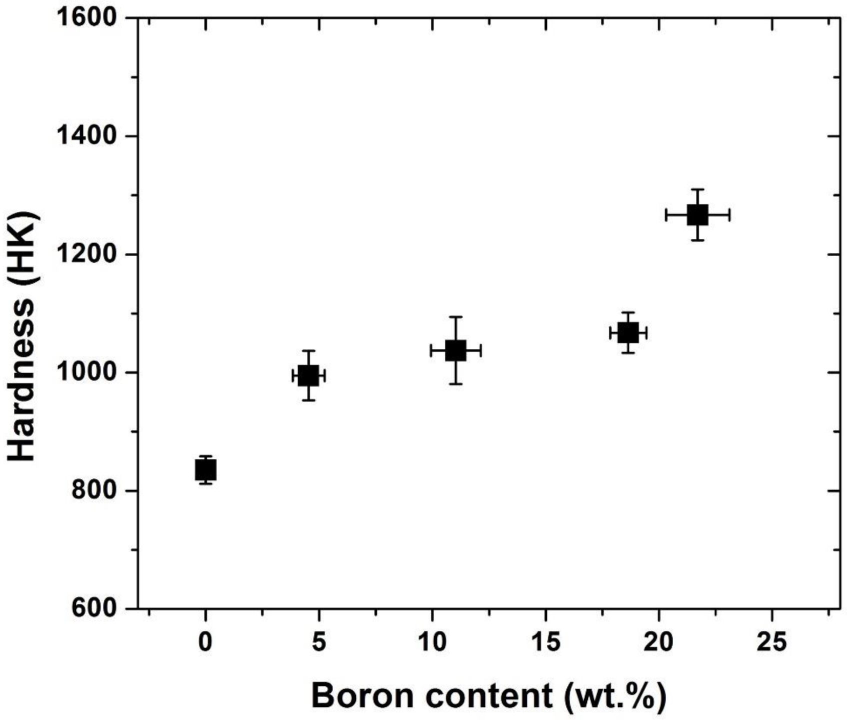

Figure 8. Hardness of Ni-W coating and Ni-W/B nanocompoite coatings presented as a function of the boron content in the deposits.

To better understand the mechanism of hardness enhanced for the obtained coatings, the relationship between boron content in coatings and hardness is shown in Fig. 8. From Fig. 8, it can be seen that the hardness depended on the boron content: composite coatings with higher boron content shows higher hardness. For the hardness of composite coatings, it is controlled by the percentage of incorporated particles and hardness of the matrix. In the current study, the incorporation of boron does not strongly affect the grain size and deposition rate of electrodeposted Ni-W matrix. The incorporated boron particles decrease the W content in deposits. As the previous results [10], the W is the grain refining element and can improve the hardness of Ni-W coatings. However, the current results reveal that hardness of composite coatings increase with the decrease in W content in the deposits, and the increase in boron incorporation in the coatings. Therefore, the hardness of Ni-W/B composite coatings is mainly contributed by the amounts of boron incorporation. The improvement mechanism of hardness for composite can be defined two different kinds of hardening mechanism according to the amount and size of particles, i.e., dispersion strengthening and particle strengthening [22, 26]. From the cross-sectional SEM images, the incorporation of boron particles have the sub-micron size (<1 μm), both the particle and dispersion strengthening are the mechanism in enhancing the hardness of the Ni-W/B composite coatings.

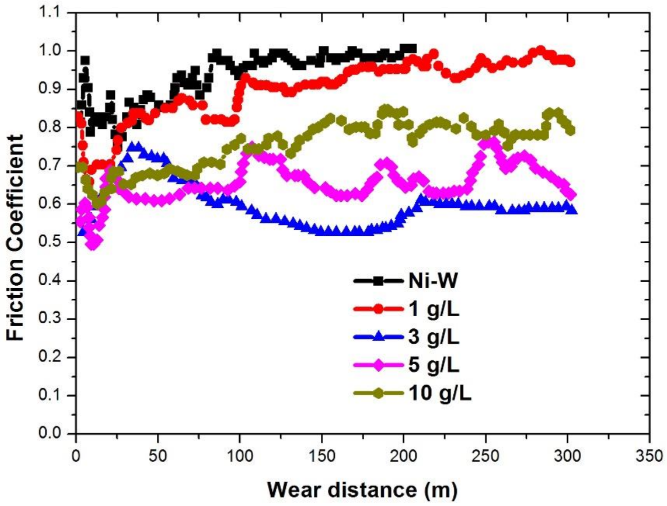

Figure 9. The friction coefficients of the Ni-W coatings and Ni-W/B composite coatings prepared with different boron concentration in solution.

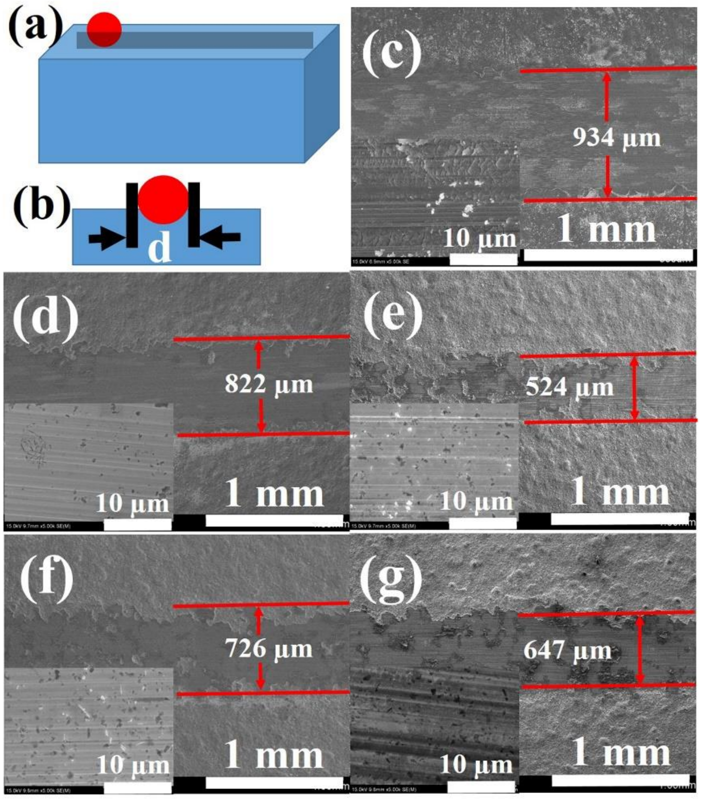

Figure 10. (a) and (b) The schematic graph of wear testing, and the general view of wear track and inside of the wear track of SEM morphology for worn surface, (c) Ni-W coatings, (d-g) Ni-W/B composite coatings prepared with different boron concentration in solution, (d) 1 g/L, (e) 3 g/L, (f) 5 g/L, (g) 10 g/L.

The wear performance was also investigated using the ball-on-disc method. The friction coefficient curves for Ni-W alloy and Ni-W/B composite coatings with boron concentration of 1, 3, 5, and 10 g/L, are shown in Fig. 9. From the friction coefficient results, it can be clearly seen that the friction coefficient of Ni-W/B composite coatings is lower than that of Ni-W coatings. Furthermore, the lowest friction coefficient is obtained for the Ni-W/B composite coating with boron concentration of 3 g/L. These results can indicate that the Ni-W/B composite coatings would be better wear performance that that of Ni-W coatings.

The schematic graph of wear testing and SEM images of wear track are presented in Fig. 10. Fig. 10(a, b) shows the schematic graph for the wear testing. Since the hardness of Si_3N_4 ball is higher than those of coatings, the ball can easily scratch the surface of coatings, resulting the wear track. The wear resistance means the coatings for resistance to damage from normal wear or usage, thus the lower wear resistance of coatings would be generated large wear track. The wear track can be seen in Fig. 10 (c-g), and the surface area of wear track can be calculated to be 18.68, 16.44, 10.48, 14.52, and 12.94 mm^2, for Ni-W and Ni-W/B composite coatings with boron concentration in solution 1, 3, 5, and 10 g/L, respectively. It indicates that the wear resistance of Ni-W coatings is lower than those of all Ni-W/B composite coatings, and the best wear performance can be obtained for the Ni-W/B composite coatings prepared at boron concentration in solution of 3 g/L.

In addition, the SEM images of inside wear tracks of Ni-W coatings and Ni-W/B composite coatings are inserted in the corresponded SEM images of Fig. 10 (c-g). For the Ni-W coatings, the worn morphology implies that the wear mechanism is mainly contributed by the abrasive and adhesive wear (Fig. 10(c)). Furthermore, the worn morphologies of Ni-W/B composite coatings show that a smoother surface than that of Ni-W coatings can be obtained. The abrasive grooves on these enlarged SEM images of Ni-W/B composite coatings were almost disappeared. This result could be attributed by the polishing effect of the boron particles grinding the frictional surface of Ni-W/B coatings.

The current work developed one efficient method to prepare Ni-W/B hard coatings with high boron content. The electroplating conditions applied in the present study show that Ni-W/B composite coatings could be deposited from Ni-W plating bath with amorphous boron particles suspension. The higher boron content in the deposits can be easily obtained (~21.7 wt.%) than those of Ni-W-B coatings prepared from sodium borate (~1.86 wt.%) [27, 28] (~1 wt.%) [29], and dimethylamino borane (~1 wt.%) [30, 31], (~3 wt.%) [32]. Several works have also reported the hardness of as-deposited Ni-W-B coatings. For example, Ni-W-B coatings could get a hardness of around 600-875 Hv[27, 28], 600-850 Hv[30-32], prepared from sodium borate, and dimethylamine borane, respectively. While in the present work, the higher hardness (994-1266 HK) of Ni-W/B composite coatings can be easily obtained from Ni-W plating bath with amorphous boron suspension. Furthermore, the previous study also demonstrated that the Ni-W-B coatings contain 1 wt.% boron can be chromium replacement alloys[29], the current results are much higher than that of boron content. Therefore, the developed method can be potential alternative chromium coatings.

4. CONCLUSIONS

In summary, electrodeposited Ni-W/B composite coatings were successfully prepared by dispersing the boron particles in the Ni-W bath. With boron incorporation, the W content in the deposits decreases and grain size of coatings slight changes. The boron content in the composite coatings increases with the increase in its concentration in the bath up to 5 g/L, beyond which it decreases. The maximum boron content in the electrodeposited Ni-W matrix is about 21.7 wt.%. The Ni-W/B coatings consist of a hard metal matrix and hard boron particles, and thus exhibit high hardness. The hardness of Ni-W/B composite coatings is mainly contributed by the boron content in deposits. A high hardness of 994-1266 HK was obtained in Ni-W/B composite coatings which is comparable to that of hard chromium plated coatings.

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References

1. A. Grosjean, M. Rezrazi, J. Takadoum, P. Berçot, *Surf. Coat. Tech.* 137 (2001) 92.
2. A.F. Zimmerman, G. Palumbo, K.T. Aust, U. Erb, *Mater. Sci. Eng. A* 328 (2002) 137.
3. W.X. Chen, J.P. Tu, L.Y. Wang, H.Y. Gan, Z.D. Xu, X.B. Zhang, *Carbon* 41 (2003) 215.
4. H. Li, Y. He, Y. Fan, W. Xu, Q. Yang, *RSC Advances* 5 (2015) 68890.
5. H. Ogihara, M. Safuan, T. Saji, *Surf. Coat. Tech.* 212 (2012) 180.
6. J. Qin, X. Zhang, Y. Xue, M. Kumar Das, A. Thueploy, S. Limpanart, Y. Boonyongmaneerat, M. Ma, R. Liu, *Surf. Interface. Anal.* 47 (2015) 331.
7. X. Zhang, J. Qin, M.K. Das, R. Hao, H. Zhong, A. Thueploy, S. Limpanart, Y. Boonyongmaneerat, M. Ma, R. Liu, *Sci. Rep.* 6 (2015) 22285.
8. T.J. Rupert, C.A. Schuh, *Acta Mater.* 58 (2010) 4137.
9. N. Sunwang, P. Wangyao, Y. Boonyongmaneerat, *Surf. Coat. Tech.* 206 (2011) 1096.
10. C.A. Schuh, T.G. Nieh, H. Iwasaki, *Acta Mater.* 51 (2003) 431.
11. A.J. Detor, C.A. Schuh, *Acta Mater.* 55 (2007) 371.
12. X. Zhang, J. Qin, T. Perasinjaroen, W. Aeksen, M.K. Das, R. Hao, B. Zhang, P. Wangyao, Y. Boonyongmaneerat, S. Limpanart, M. Ma, R. Liu, *Surf. Coat. Tech.* 276 (2015) 228.
13. K.-H. Hou, T. Han, H.-H. Sheu, M.-D. Ger, *Appl. Surf. Sci.* 308 (2014) 372.
14. Y. Boonyongmaneerat, K. Saengkiettiyut, S. Saenapitak, S. Sangsuk, *Surf. Coat. Tech.* 203 (2009) 3590.
15. K.-H. Hou, Y.-C. Chen, *Appl. Surf. Sci.* 257 (2011) 6340.
16. Y. Wang, Q. Zhou, K. Li, Q. Zhong, Q.B. Bui, *Ceram. Int.* 41 (2015) 79.
17. J. Qin, T. Irifune, H. Dekura, H. Ohfuji, N. Nishiyama, L. Lei, T. Shinmei, *Phys. Rev. B* 85 (2012) 014107.
18. J. Qin, N. Nishiyama, H. Ohfuji, T. Shinmei, L. Lei, D. He, T. Irifune, *Scripta Mater.* 67 (2012) 257.
19. A. Robin, J.C.P. de Santana, A.F. Sartori, *Surf. Coat. Tech.* 205 (2011) 4596.
20. S.H. Yeh, C.C. Wan, *Mater. Sci. Tech-lond.* 11 (1995) 589.
21. C. Müller, M. Sarret, M. Benballa, *Surf. Coat. Tech.* 162 (2003) 49.
22. K. Krishnaveni, T.S.N. Sankara Narayanan, S.K. Seshadri, *J. Alloy. Compd.* 466 (2008) 412.

23. H. Ogihara, M. Safuan, T. Saji, *Surf. Coat. Tech.* 212 (2012) 180.
24. O. Younes, L. Zhu, Y. Rosenberg, Y. Shacham-Diamand, E. Gileadi, *Langmuir.* 17 (2001) 8270.
25. M.-C. Chou, M.-D. Ger, S.-T. Ke, Y.-R. Huang, S.-T. Wu, *Mater. Chem. Phys.* 92 (2005) 146.
26. U. Lagerpusch, E. Nembach, *Scripta Mater.* 42 (2000) 615.
27. M.G. Hosseini, M. Abdolmaleki, H. Ebrahimzadeh, S.A. Seyed Sadjadi, *Int. J. Electrochem. Sci.* 6 (2011) 1189.
28. M.G. Hosseini, M. Abdolmaleki, S.A. Seyed Sadjadi, *Protection of Metals and Physical Chemistry of Surfaces* 46 (2010) 117.
29. C.P. Steffani, J.W. Dint, J.R. Groza, A. Palazoglu, *J. Mater. Eng. Perform.* 6 (1997) 413.
30. F.-Z. Yang, Z.-H. Ma, L. Huang, S.-K. Xu, S.-M. Zhou, *Chin. J. Chem.* 24 (2006) 114.
31. G. Graef, K. Anderson, J. Groza, A. Palazoglu, *Mat. Sci. Eng. B* 41 (1996) 253.
32. T. Nagai, K. Hodouchi, H. Matsubara, *Surf. Coat. Tech.* 253 (2014) 109.