Electrodeposition, microstructure and property of Co–WC composite coatings

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Abstract

A novel Co–WC composite coating was fabricated on the surface of high-speed steel (HSS) substrate by direct current (DC) electrodeposition. The co-electrodeposition mechanism of Co–WC composite coating was explored. Furthermore, the effects of process parameters on the microstructure and micro-hardness of the coating were studied. The microstructure and composition of Co–WC composite coating were investigated by scanning electron microscopy equipped with an energy dispersive x-ray spectroscope. The adhesion strength of Co–WC composite coating was evaluated by WS-2005 automatic scratch tester. Results revealed that WC particles were homogeneously embedded in the Co matrix with few defects, and the Co–WC composite coating was firmly bonded to the HSS substrate. The optimized parameters are as follows: WC concentration of 35 g l⁻¹, current density of 6.5 Adm⁻², stirring rate of 300 rpm, and pH of 7.5 and temperature of 50 °C. X-ray diffraction analysis indicated that the Co matrix combined physically with the WC particles. Also, the microindentation hardness of Co–WC composite coating was tested by micro-hardness tester. It was found that the microindentation hardness of Co–WC composite coating reached the maximum value of 542 HV under the optimal process conditions.

1. Introduction

Metals possess good plasticity and toughness. However, the relatively low hardness is the bottleneck of its wide application in engineering. In recent years, metal matrix composite coatings reinforced with inert ceramic particles have drowned tremendous attraction in effectively improving the performance of metal substrate [1–5]. Because of its promising mechanical properties, such as high hardness and wear resistance, cermet composite coating has been widely used in manufacturing industry of machining, drilling, forming dies and wearing parts. The general methods for the preparation of cermet composite coating are high velocity oxygen fuel (HVOF) spraying [6–9], plasma spraying [10, 11] and vacuum sputtering [12], etc. While, there are several limitations in the previous approaches, such as complex technique and high temperature, which lead to particle oxidation and low bonding strength, thus reducing the overall performance of the composite coatings. Consequently, the scientific community is increasingly interested in developing advanced technologies for preparing ceramic reinforced composite coating on various substrates, while maintaining their excellent properties to prevent degradation under severe environmental conditions.

Electrodeposition methods [13–15] have been widely developed to fabricate uniform and crack free metal matrix ceramic composite coating, due to its merits of low temperature as well as the simplicity of the experimental setup. Cu–SiC composite coating [16] was fabricated by DC electrodeposition from the electrolytic bath containing 1.5 g l⁻¹ saccharin. Ni/Cr,C₂–NiCr composite coating [17] was successfully prepared on copper alloy, and the effect of Cr₃C₂ particles on the mechanical properties of the composite coatings was investigated. Mercier et al [18] produced Ni–SiC composite coating on the steel substrate by DC electrodeposition. It is well-known that the successful electrodeposition is based on a stable dispersion system,
which is used for the directional movement of insoluble particles under an applied electric field [19]. However, previous studies have revealed that ceramic particles are easy to agglomerate, which seriously damages the properties of the composite coating. Therefore, it is necessary to investigate the influence of process parameters (such as particle concentration, stirring rate, temperature, etc.) on the microstructure and properties of Co–WC composite coating.

On the basis of aforementioned consideration, the aim of this study is the preparation of Co–WC composite coating on HSS substrate by DC electrodeposition. In order to further understand the process of electrodeposition, the growth mechanism of Co–WC composite coating was explored. Herein, it was investigated on the microstructure, WC content, deposition rate and microindentation hardness of the coating, and the experimental conditions were optimized. This work is expected to pave the path for the widespread application of Co–WC composite coating.

2. Experimental methods

2.1. Preparation of Co–WC composite coatings

The setup used in this experiment comprised an electrolytic cell system. HSS (W18Cr4V) substrates with a size of 22 mm × 20 mm × 6 mm were polished initially with abrasive paper of 320, 600, 800, 1200 grit by sequence to remove oxides. The substrate was cleaned in acetone with an ultrasonic cleaner for 10 min and then suspended in alkaline solution for 15 min to eliminate grease. In order to remove residual alkaline solution, the treated substrate was rinsed with deionized water and dried in air. A piece of well cleaned HSS substrate was used as cathode which faced a Co plate anode vertically to form a parallel plate with a distance of 2 cm. The electrodeposition was carried out with DC power. The process is briefly exhibited in figure 1. The chemical compositions of the alkaline solution are listed table 1. The process parameters of co-electrodeposition are shown in table 2.
2.2. Characterization
The morphology of Co–WC composite coating was observed by scanning electron microscopy (SEM) equipped with an energy dispersive x-ray spectroscope (EDS). The x-ray diffraction (XRD) patterns of the coating were achieved by x-ray diffractometer using Cu Kα radiation (Kα = 0.15406 nm). WS-2005 automatic scratch tester was used to evaluate the adhesion strength of Co–WC composite coating by the critical load. During the test, the radius of curvature of the tip of the diamond indenter for loading is 200 μm, the cone angle is 120°, the test load is 80 N, the loading rate is 80 N m⁻¹, the scratch length is 4 mm, and the operation mode is dynamic load.

The microindentation hardness tests using EM-1500L micro-hardness tester were performed under a load of 100 gf with a dwell time of 5 s. The microindentation hardness value was derived from an average of five measurements.

3. Results and discussion

3.1. Co-electrodeposition mechanism
In order to further understand the co-electrodeposition mechanism, the growing process of Co–WC composite coating depicted in figure 2 was discussed. According to Guglielmi’s electrodeposition model [20–23], the growth process of Co–WC composite coating is divided into four stages. The first stage is mass transfer. When CoSO₄·7H₂O and WC particles are added in the aqueous solution, WC particles with many Co²⁺ adsorbed on the surface are stably suspended in the electrolytic bath by the cavitation effect of ultrasonic wave. Under the action of electric field and forced convection, cobalt ions and WC particles with cobalt ionic cloud move to the cathode surface. In the diffusion layer near the cathode surface, hard particles and cobalt ions pass through the diffusion layer are physically adsorbed on the cathode surface by Van der Waals

| Reagents and parameters | Concentration and operating conditions |
|------------------------|-----------------------------------------|
| CoSO₄·7H₂O (cobalt sulfate heptahydrate) | 150 g l⁻¹ |
| NaCl (sodium chloride) | 40 g l⁻¹ |
| H₃BO₃ (boracic acid) | 75 g l⁻¹ |
| WC | 0–45 g l⁻¹ |
| PH | 7.5 |
| Temperature | 55 °C |
| Current density | 3.5–11 Adm⁻² |
| Stirring rate | 0–500 rpm |
| Plating time | 2 h |

Figure 2. Schematic diagram of the growing process of Co–WC composite coating.
forces. Subsequently, the third stage is reduction. Because of the strong Helmholtz electric field on the cathode surface, Co$^{2+}$ is reduced by electron transfer, thus forming a strong adsorption on the cathode surface. Finally, WC particles are firmly embedded in the growing Co matrix to form a Co–WC composite coating.

3.2. Surface morphologies of Co–WC composite coatings

3.2.1. Influence of current density on surface morphologies of composite coatings

The surface morphologies of Co–WC composite coatings prepared at various current densities are shown in figure 3. It can be seen that the change in current density has a significant effect on the microstructure of the coating. To the best of our knowledge, a structurally dense composite coating represents superior performance. Know from the figures 3(a)–(c), as the current density increases to 6.5 $\text{Adm}^{-2}$, the island-like structure formed on the surface of the coating is reduced, and the uneven surface morphology is replaced by a smooth, cauliflower-like microstructure. The increase in current density can effectively increase the nucleation rate of Co matrix, which results in grain refinement. Furthermore, the deposition rate of Co matrix and WC particles may
not be different in this condition, so the hard particles are homogeneously distributed in the Co matrix. Figures 3(d)–(f) show the surface morphologies of the Co–WC composite coatings prepared at current densities of 8 Adm$^{-2}$, 9.5 Adm$^{-2}$ and 11 Adm$^{-2}$, respectively. As the current density is further increased, the coating presents a rough morphology with many defects such as holes and cracks. The fact is that WC particles tend to agglomerate at high current density. Based on the Derjaguin-Landau-Verwey-Overbeek (DLVO) theory [24], when the current density exceeds the optimal value, the hydrogen evolution reaction of the cathode increases, which leads to the decrease of zeta potential of the suspended particles, so the repulsion between particles is reduce. Finally, WC particles agglomerate and then embed into the growing Co matrix, which seriously deteriorates the coating quality. Now it is believed that the Co–WC composite coating with current density of 6.5 Adm$^{-2}$ is the best.

3.2.2. Influence of WC concentration on surface morphologies of the Co–WC composite coatings

Figure 4 presents the surface morphologies of Co–WC composite coatings prepared from the electroplating bath containing diverse WC concentrations. From figure 4(a), upon the introduction of WC particles, the nodular protrusions are formed on the surface of Co–WC composite coating, and Co grains present an abnormal needle-like structure. This may be related to the WC incorporation in the grain interface, which obstructs the growth of
cobalt grains. Moreover, because of the ‘tip discharge effect’ [22], cobalt ions are preferentially adsorbed at the tip and reduced to atoms, thus forming the protrusion structure. Comparing cobalt grains. Moreover, because of the deposition rate of Co results in an increase in the number of catalytically active sites, which accelerates the deposition of Co matrix. At.

3.3. Cross-sectional morphology and composition of the Co–WC composite coatings
The cross-sectional morphology of Co–WC composite coating is demonstrated in figure 5(a). As can be seen distinctly, the gray-white section on the below is the Co–WC composite coating, and the gray section on the above is the HSS substrate. WC particles are homogeneously dispersed in the Co matrix without visible impurities. Figure 5(b) shows the acoustic emission spectra of Co–WC composite coating synthesized from electrolytic bath containing different WC concentrations. It can be observed that the critical load of the composite coating prepared at the WC concentration of 35 g l\(^{-1}\) reaches the maximum value of 67.5 N, which indicates that the Co–WC composite coating has a good combination with the substrate. The energy spectrum analysis of Co–WC composite coatings is shown in figures 6(a)–(c), the results show that the Co–WC composite coating was successfully fabricated on the surface of HSS substrate, and the coating contains three elements of tungsten, cobalt and carbon.

Figure 7 illustrates the XRD patterns of Co and Co–WC coatings. By comparison, many diffraction peaks of WC appear at the 2\(\theta\) = 31.462°, 36.602° and 48.262° with (001), (100), and (101) miller indices, respectively. It is apparent from figure 7 that there is no other phase in the Co–WC composite coating, which proves that the WC particles and Co matrix are mechanically bonded. Furthermore, as demonstrated in the patterns, the diffraction peaks of Co appear at the 2\(\theta\) = 41.674°, 44.50° and 76.366° with (001), (002) and (110) miller indices, respectively. The result indicates that the coating has a typical polycrystalline structure, and the growth trends on these crystal faces are not much different.

3.4. WC content and deposition rate of Co–WC composite coatings
3.4.1. The effect of WC concentration
Figure 8 demonstrates the WC content and deposition rate of Co–WC composite coating as a function of WC concentration. It is obvious that the maximums of WC content and deposition rate are achieved under the condition of WC concentration of 35 g l\(^{-1}\). Changing WC concentration can provide low WC content and deposition rate of Co–WC composite coating. As the WC concentration increases, the adsorption rate of hard particles on the cathode surface increases, which promotes the incorporation of WC particles. When the WC concentration increases to 35 g l\(^{-1}\), the phenomenon that the WC content in the Co–WC composite coating exhibits the maximal value of 18.4 wt%, which could be interpreted that the particles suspended in the electrolytic bath reach saturation state, and then uniformly embed into the Co matrix, so the composite coating displays high load of WC. Moreover, the increased scouring effect of WC particles on the electrode surface results in an increase in the number of catalytically active sites, which accelerates the deposition of Co matrix. At
the same time, the incorporation of WC increases the effective deposition region of cobalt matrix [26]. Therefore, the deposition rate of Co–WC composite coating is dramatically increased. However, as the WC concentration is further increased, WC particles are prone to agglomeration and sedimentation, resulting in the reduction of effective deposition area of Co matrix. Besides, excessive WC particles form a shielding effect that prevents the directional movement of the particle.

The effect of current density
The variation in the WC content and deposition rate of Co–WC composite coating prepared at various current densities shows in figure 9. With the increase of current density from 3.5 Adm$^{-2}$, the WC content and deposition rate of the coating first increase, and then exhibit the maximum at the current density of 6.5 Adm$^{-2}$, and finally decline.

The nucleation of Co matrix dominates the electrodeposition process at high current density [27]. The enhancement of current density leads to the increase in electromigration rate and cathode reduction rate of Co
matrix, which significantly improves the deposition rate of Co–WC composite coating and promotes the implantation of ceramic particles into the coating.

Nonetheless, as the current density exceeds the optimal value of 6.5 Adm$^{-2}$, turbulence occurs in the electrolytic bath, which hinders the movement of cobalt ions to the cathode, so the deposition rate of the composite coatings decreases. In addition, too high current density will aggravate the side reaction of cathode, resulting in the formation of H$_2$ film on the cathode surface, which seriously impedes the deposition of WC particles and Co$_2^+$. Additionally, due to the impact of hydrogen, WC particles physically adsorbed on the cathode surface may fall off.

**The effect of stirring rate**

Mechanical agitation plays an important role in avoiding the agglomeration and sedimentation of suspended particles. It can effectively eliminate the concentration polarization, release hydrogen bubbles attached to the cathode surface and keep the uniform temperature distribution.

From the graph of WC content and deposition rate of Co–WC composite coating with diverse stirring rate illustrated in figure 10, we can see that the WC content and deposition rate of the coating increase first and then decrease with the increase of stirring rate. As the stirring rate is increased, the force generated by mechanical stirring can promote the movement of suspended WC particles to the cathode and accelerate the separation of bubbles from the cathode surface, thus promoting the growth of Co–WC composite coating. Nevertheless, at high stirring rates (>300 rpm), some pre-deposited WC particles (weak adsorption) detach from the cathode surface, which reduces the WC incorporation and deposition rate of the coating. In addition, because of the collision between particles, the surface energy of particles may increase, which leads to the agglomeration and
settlement of WC particles, so the reduction in the WC content and deposition rate of Co–WC composite coating is driven in part by this fact.

3.5. Microindentation hardness of Co–WC composite coating

The composition and grain size of the coating, the microstructure as induced by WC incorporation, and the content and distribution of WC are important factors affecting the mechanical properties of Co–WC composite coating.

The microindentation hardness of Co–WC composite coatings prepared by different process parameters is shown in figures 11–13. As it is observable, the microindentation hardness of Co–WC composite coating reaches the maximum of 542 HV under the conditions of WC concentration of 35 g l$^{-1}$, current density of 6.5 Adm$^{-2}$ and stirring rate of 300 rpm. Besides, the microindentation hardness of HSS substrate is only 176 HV, which proves that the Co–WC composite coating can effectively protect the HSS substrate. The improvement in microindentation hardness of Co–WC composite coating could be explained on the basis of fine-grained strengthening and dispersion strengthening. According to Hall-Petch effect [28], the inverse relationship between grain size and micro-hardness is verified. WC particles provide an obstacle to the movement of dislocations, which leads to the increase of the resistance of plastic flow, thus increasing the microindentation hardness.
hardness of Co–WC composite coating [29]. Furthermore, the inherent mechanical strength of WC particles plays an indispensable role in improving the microindentation hardness of Co–WC composite coatings.

However, the microindentation hardness of the coating is significantly reduced by changing the optimal process parameters, which is attributed to the decrease of WC content in the coating and the appearance of many defects such as cracks and holes. As already mentioned, it is believable that the WC content and microstructure of Co–WC composite coating have an important influence on the microindentation hardness of the coating (as investigated in sections 3.2 and 3.4).

4. Conclusions

1. Co–WC composite coatings were successfully prepared on the surface of HSS substrates by DC electrodeposition. By optimizing the parameters of electrodeposition, the critical load of coating damage
reached the maximum value of 67.5 N, and the WC content as well as deposition rate of Co–WC composite coating achieved the maximal value of 18.4 wt% and 56.3 μm/h, respectively.

2. WC particles were homogeneously incorporated into Co matrix under the optimal process parameters, and the microindentation hardness of Co–WC composite coating exhibited the maximum of 542 HV.

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References

[1] Rezaee M, Razavi M, Zakeri M, Rahimipour M R and Nikzad I 2018 Fabrication of functionally graded Fe–TiC wear resistant coating on CK45 steel substrate by plasma spray and evaluation of mechanical properties Ceram. Int. 44 22378–86
[2] Bhat A and Bourell D 2015 Tribological properties of metal matrix composite coatings produced by electrodeposition of copper Mater. Sci. Technol. 31 969–74
[3] Jarząbek D M, Dziedziński C, Dera W, Chrzanoska J and Wojciechowski T 2018 Influence of Cu coating of SiC particles on mechanical properties of Ni/SiC co-electrodeposited composites Ceram. Int. 44 21750–8
[4] Li B, Du S and Mei T 2019 Pulse electrodeposited Ni–Cu–TiAlN–ZrO2 nanocomposite coating: microstructural and electrochemical properties Mater. Res. Express 6 096433
[5] Mardi K B, Dnist A R, Mallick A and Reddy A R 2018 Effect of Al2O3 nanoparticles on tribological behaviour of Mg-6Al alloy-based nanocomposites Int. J. Surf. Sci. Eng. 12 402–18
[6] Duan X, Zhang X, Ke C, Jiang S, Wang X, Li S, Guo W and Cheng X 2017 Microstructure and optical properties of Co–WC–Al2O3 duplex ceramic metal–diesel solar selective absorbing coating prepared by high velocity oxy-fuel spraying and sol–gel method Vacuum 145 209–16
[7] Zoëi M S, Sadeghi M H and Salehi M 2016 Effect of grinding parameters on the wear resistance and residual stress of HVOF-deposited WC–10Co–4Cr coating Surf. Coat. Technol. 307 886–91
[8] Berger L M 2015 Application of hardmetals as thermal spray coatings Int. J. Refrac. Met. Hard Mater 49 350–64
[9] Somasundaram B, Kadoli R, Ramesh M R and Ramesh C S 2016 High temperature corrosion behaviour of HVOF sprayed WC–CrC–Ni coatings Int. J. Surf. Sci. Eng. 10 400–13
[10] Sun X, Huang J, Yang J and Chen S 2019 Microstructure evolution and mechanical properties of in situ bimodal TiC–Fe coatings prepared by reactive plasma spraying Ceram. Int. 45 8584–57
[11] Ahmadi M S, Shoja-Razavi R, Valerie Z and Jamali H 2019 Evaluation of hot corrosion behavior of plasma sprayed and laser glazed YSZ–Al2O3 thermal barrier composite Opt. Laser Technol. 111 687–95
[12] Greczynski G, Mrad S, Hultman L and Schneider J M 2016 Unintentional carbide formation evidenced during high-vacuum magnetron sputtering of transition metal nitride thin films Appl. Surf. Sci. 385 156–9
[13] Corni I, Ryan M P and Boccaccini A R 2008 Electrophoretic deposition: from traditional ceramics to nanotechnology J. Eur. Ceram. Soc. 28 1353–67
[14] Singh B P, Nayak S, Nanda K K, Jena B K, Bhattacharjee S and Besra L 2013 The production of a corrosion resistant graphene reinforced composite coating on copper by electrophoretic deposition Carbon 61 47–56
[15] Claudel F, Stein N, Allain N, Tidu A, Hajczak N, Lallemant R and Close D 2019 Pulse electrodeposition and characterization of Zn–Mn coatings deposited from additive-free chloride electrolytes J. Appl. Electrochem. 49 399–411
[16] Mirsaidee-Ghazi S M, Allahkarim S R and Molaei A 2019 Development and investigation of Cu/SiC nano-composite coatings via various parameters of DC electrodeposition Tribol. Int. 134 221–31
[17] Hosseinzadeh M, Jafari A, Esmaeilzadeh M and Mirzaei A 2018 Morphological and mechanical characterization of co-deposited Ni/Cr/C2–NiCr composite coatings Mater. Res. Express 6 086517
[18] Mercier D, Vanhumbeeck J F, Caruso M, Eynde X V and Febvre M 2019 Microstructural and mechanical characterisation of electroplated nickel matrix composite coatings Surf. Eng. 35 178–89
[19] Zhang D and Li X 2015 Fabrication and kinetics study of nano-Al/NiO thermite film by electrophoretic deposition Mater. Sci. Eng. A 119 4688–94
[20] Bercot P, Pena-Munoz E and Pagetti J 2002 Electrolytic composite Ni–PTFE coatings: an adaptation of Guglielmi’s model for the phenomena of incorporation Surf. Coat. Technol. 157 282–9
[21] Ahmadiyeh S, Rasooli A and Hosseini M G 2019 Ni–B/SiC nanocomposite coating obtained by pulse plating and evaluation of its electrochemistry and mechanical properties J. Surf. Eng. 35 861–72
[22] Li B S and Zhang W W 2019 Facile synthesis and electrochemical properties of a novel Ni–B/TiC composite coating via ultrasonic-assisted electrodeposition Ultrason. Sonochem. 61 104837
[23] Li B, Li D, Mei T Y, Xia W Z and Zhang W W 2019 Fabrication and characterization of boron nitride reinforced Ni–W nanocomposite coating by electrodeposition J. Alloys Compd. 777 1234–44
[24] Li C C, Chang J, Wu C W, Chang C W and Yu R H 2017 Newly designed diblock dispersant for powder stabilization in water-based suspensions J. Colloid Interface Sci. 506 180–7
[25] Dong Y R, Sun W C, Liu X J, Jia Z W, Guo F, Ma M and Ruan Y Y 2019 Effect of CNTs concentration on the microstructure and friction behavior of Ni-GO-CNTs composite coatings Surf. Coat. Technol. 359 141–9
[26] Wang Y, Sun W C, Wang C A, Huang Y and Xu J M 2017 Microstructure, friction, and wear properties of Ni–Al2O3–MoS2 composite coatings Int. J. Appl. Ceram. Technol. 14 889–98
[27] He Z, Hayat M D, Yuan X, Wang X and Cao P 2018 Effects of deposition time and current density on PbO2 electrosynthesis from methanesulfonate electrolyte J. Appl. Electrochem. 48 783–91
[28] Gao Z, Hu K, Zhang T and Li J 2015 Fine grained microstructure crystallographic feature and its effect on mechanical behavior in Ni–Cr–W superalloy Mater. Sci. Eng. A 639 107–13
[29] Chen J, Li J, Xiong D, He Y, Ji Y and Qin Y 2016 Preparation and tribological behavior of Ni-graphene composite coating under room temperature Appl. Surf. Sci. 361 49–56