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ARTICLE

Preparation of FeCoNiCr High Entropy Alloy Coatings and Optimization of Process Parameters

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Abstract: FeCoNiCr high entropy alloy coatings were prepared by electrodeposition in sulfate system with citric acid and sodium citrate as the complexing agent. The effects of current density, bath temperature, and pH value on the composition, morphology, crystal structure and hardness of the coatings were studied. The results show that the prepared FeCoNiCr high entropy alloy coatings are amorphous and uniform. The optimized process parameters are: pH=2.5, temperature of 25 °C, and current density of 25 A·dm^{-2}.

Key words: FeCoNiCr high entropy alloy; electrodeposition; morphology; crystal structure; hardness

With the development of electroplating industry, the research and application of alloy coatings are increasingly extensive[1]. Alloy coatings can change the properties of substrate materials, but the traditional alloy system cannot meet the requirement of application. There are many factors restricting the development. As an innovative alloy system, high entropy alloys have attracted significant attention due to their excellent properties[2-5]. High entropy alloys are solid solution strengthened alloys with 4~13 elements[6-10]. Because of the cocktail effect, the structure and properties of the alloys are improved by adding one or more elements. The wear resistance and corrosion resistance of FeCoNiCr high entropy alloy coatings are better than those of the ternary alloy coatings. At present, the most common preparation methods of high entropy alloy are laser cladding and mechanical alloying[11,12]. However, FeCoNiCr high entropy alloy prepared by electrodeposition is barely investigated, remaining many problems to be further addressed. When the elements are mixed at the same molar ratio, the alloy hardness is higher and the corrosion resistance is better. However, due to the mutual restriction of the deposition of various elements and the component of different alloys, intermetallic compounds form easily, increasing the alloy brittleness[13]. In this research, Co was added to FeNiCr ternary alloy coatings as a main element because of its excellent hardness, wear resistance, and electrochemical behavior[14]. The electronegativity of Fe, Co, Ni, and Cr is 1.83, 1.88, 1.91, and 1.66, respectively, among which the electronegativity of Cr is the lowest. The influence of current density (D_K) is related to the electronegativity. After adding sodium citrate and citric acid to combine with various ions in the plating bath, the electronegativity is higher, the composite is more stable, and the relative stability of Cr^{3+} composite is relatively lower. During the electrodeposition process, it is easy to dissociate Cr^{3+}, making its precipitation potential equal or close to that of other metal ions and achieving the purpose of co-deposition. FeCoNiCr high entropy alloy coatings were deposited in sulfate system by electrodeposition. The effects of D_K, bath temperature (T), and pH value on the composition and hardness of the coatings were studied. The surface morphology and crystal structure of the coatings were analyzed.

1 Experiment

To improve the surface quality of plating substrate, a commercially available copper plate with the dimension of 20 mm×20 mm was used as the substrate. The substrate was firstly immersed in a solution of 16vol% H_2SO_4 and 8vol% H_2O_2 to remove the copper oxide on the surface. Then it was immersed in a solution with 15 g·L^{-1} NaOH, 25 g·L^{-1} Na_2CO_3, and 25 g·L^{-1} Na_3PO_4 to remove the cutting oils. Further, it was washed by hot water of 60 °C and cold water, separately, and then weakly etched by a 5vol% H_2SO_4 solution for 30 s.

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Finally, it was washed with deionized water.

The materials of 200 gL^{-1} $Cr_2(SO_4)_3·6H_2O$, 2 gL^{-1} $FeSO_4·7H_2O$, 4 $g·L^{-1}$ $CoSO_4·7H_2O$, 20 $g·L^{-1}$ $NiSO_4·6H_2O$, 25 $g·L^{-1}$ H_3BO_3, 75 $g·L^{-1}$ KCl, 48 $g·L^{-1}$ $Na_3C_6H_5O_7·2H_2O$, and 96 $g·L^{-1}$ $C_6H_8O_7·H_2O$ were used. D_K was in the range of 15~35 $A·dm^{-2}$, pH value varied between 1.5~3.5, and the temperature varied between 20~60 °C. A copper sheet (as the cathode material) was used for plating. Analytical reagents and deionized water were used to make the plating bath, and NaOH and H_2SO_4 were used to control the pH value.

A HS-4800 field emission scanning electron microscope (FESEM, Hitachi, East coast port city, Honshu Island) accompanied with a INC250 energy disperse spectroscope (EDS) was used to analyze the content of Fe, Co, Ni, and Cr in the FeCoNiCr high entropy alloy coatings. A FM-ARS9000 hardness tester was used to measure the hardness of alloy coatings. The applied force and time were 50 g and 15 s, respectively. The hardness value was obtained by the average of five measurements.

2 Results and Discussion

2.1 Influence of current density D_K on composition and hardness

The experiments were conducted under the condition of unchanged bath composition, pH=2.5, and electrodeposition at 25 °C for 60 min, and the influence of D_K on the composition and hardness of coatings was studied. The results are shown in Fig.1 and 2, from which the optimal D_K is obtained.

It can be seen from Fig. 1 and 2 that Cr content gradually increases and Co content gradually decreases with the increase of D_K, while the content of Fe and Ni during the electrodeposition does not change significantly. In addition, the change trend of hardness and Cr content in coatings with different current densities is the same. When D_K is 25 $A·dm^{-2}$, the elemental distribution in the coatings is homogeneous, and the contents of different elements are similar, which is an optimal state. When D_K is 15 $A·dm^{-2}$, the Cr content of the high entropy alloy coatings is 10.75at%. When D_K increases to 35 $A·dm^{-2}$, the Cr content reaches to 27.34at%. This phenomenon shows that increasing D_K can increase the Cr content in the coatings within a certain range. When D_K is low, the deposition rate and nucleation rate of the coatings are relatively slow, the grain growth is uneven, and the surface of the coatings is not dense, resulting in low hardness. With the gradual increase of D_K, the cathodic polarization is enhanced, the power of ion reaction increases, the nucleation rate accelerates, and the coating particles are refined, resulting in the increase of hardness. However, when D_K is too high, the hydrogen evolution reaction on the surface of plating piece becomes violent, and the pH value in the area near the cathode rises rapidly. As a result, the hydroxyl-bridge polymerization reaction occurs due to Cr^{3+} [15], and various hydroxyl-bridge compounds are generated. At the same time, because of the edge effect of current, the "scorch" phenomenon appears around the plating piece. In addition, the coating edge blackens and the hardness reduces.

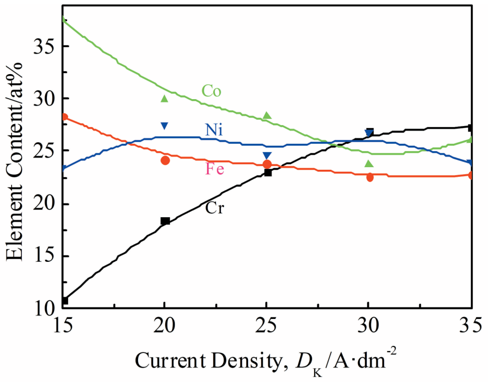

Fig.1 Relationship between element content in coatings and current density D_K

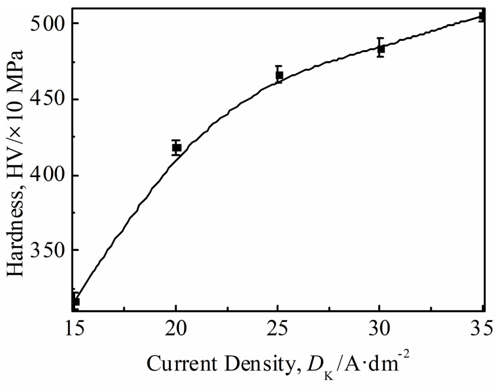

Fig.2 Relationship between hardness HV of coatings and current density D_K

The SEM images in Fig. 3 present the morphologies of FeCoNiCr alloy coatings deposited with different D_K for 60 min. The XRD patterns for the FeCoNiCr alloy coatings are shown in Fig.4.

When D_K changes between 15~35 $A·dm^{-2}$, XRD patterns (Fig.4) show a wide and blunt diffraction peak near $2\theta=45°$, and the coatings present the amorphous state. There are several microcracks on the surface (Fig.3). When D_K is low, the deposition rate is small, the obtained coatings are not smooth, and the globular grain growth is prominent. The low nucleation rate caused by low D_K results in the insufficient nucleation for grain growth. So the distribution of spherical grain on the coating surface is not uniform. As D_K increases gradually, the cathodic polarization increases, indicating that the nucleation speed of grains is faster than the growth speed, resulting in the finer grains and denser coatings. In this case, the amorphous peak shifts slightly to the left, indicating that the lattice constant increases. Generally, the increase of D_K increases the Cr content of coatings. The atomic radius of Cr is larger than that of other three elements, so FeCoNiCr high entropy alloy lattice constant increases. However, when D_K is

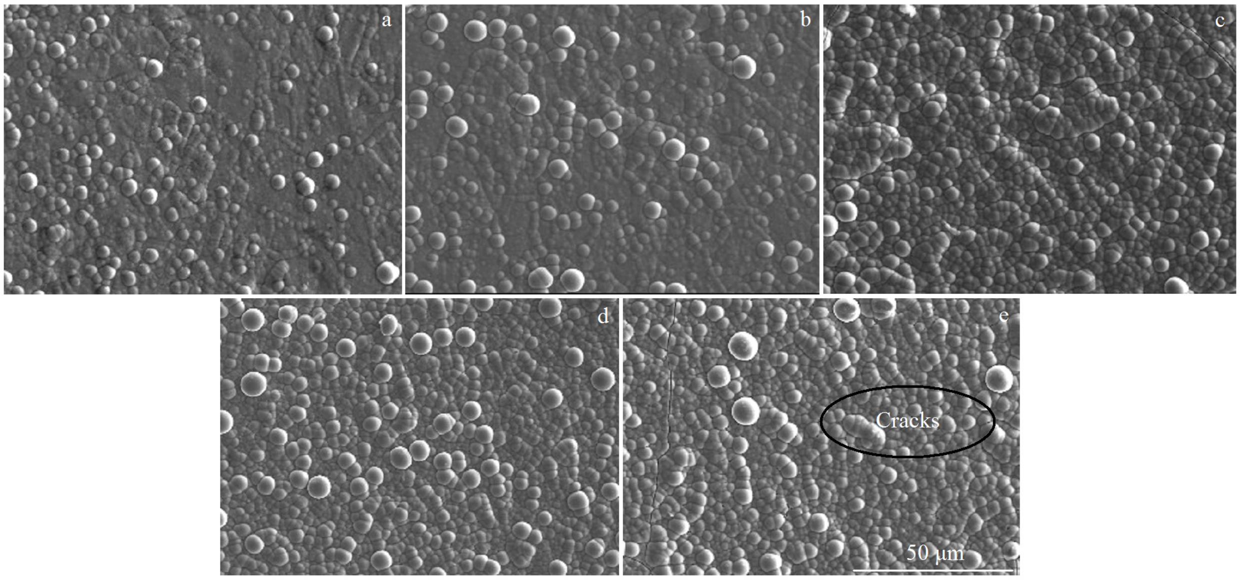

Fig.3 SEM images of FeCoNiCr coatings deposited at different current density D_K for 60 min: (a) 15 A·dm^{-2}, (b) 20 A·dm^{-2}, (c) 25 A·dm^{-2}, (d) 30 A·dm^{-2}, and (e) 35 A·dm^{-2}

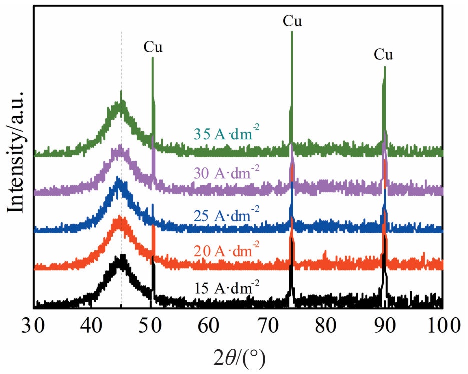

Fig.4 XRD patterns of FeCoNiCr alloy coatings deposited at different current density D_K for 60 min

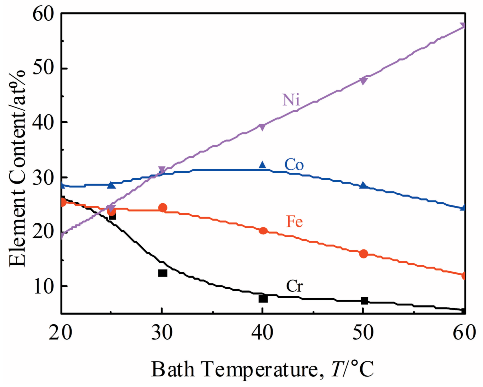

Fig.5 Relationship between element content in coatings and bath temperature T

higher than 25 A·dm^{-2}, the hydrogen evolution reaction on the surface of the sample intensifies, and the generated gas cannot be discharged in time. This causes pores and even hydrogen embrittlement in the coatings[16]. Therefore, the optimal value of D_K is 25 A·dm^{-2}.

2.2 Influence of bath temperature *T* on composition and hardness

The experiments were conducted under the condition of unchanged bath composition, pH=2.5, and current density D_K of 25 A·dm^{-2}, and the influence of the temperature T of plating bath on the composition and hardness of coatings was studied. The electrodeposition time was set as 60 min. The results are shown in Fig.5 and 6, from which the optimal T is obtained.

As shown in Fig.5 and 6, with the increase of bath temperature, Cr content of the high entropy alloy coatings decreases, Ni content increases rapidly, and the hardness of the coatings

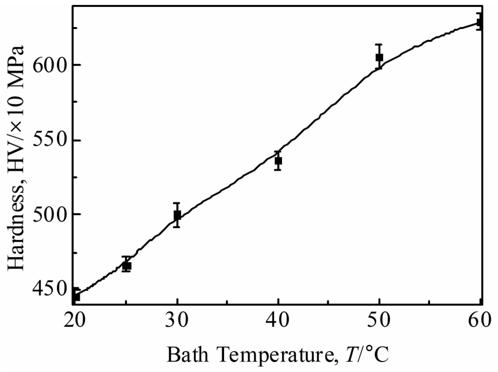

Fig.6 Relationship between hardness HV of coatings and bath temperature T

also increases. The continuously increasing trend is attributed to the decrease of Cr content in the coatings. With the increase of bath temperature, the content of Ni, which possesses high hardness, increases, resulting in the increase of hardness of the coatings. When the bath temperature is 25 ℃, the composition of high entropy alloy coatings reaches the optimization state, where the contents of each component are similar. Because the influence of temperature on the electrode potential of various ions is different, when the temperature is higher than 30 ℃, the Ni content of coatings increases obviously, the bright range of the coating surface expands, and the Cr content of the high entropy alloy coatings decreases due to the hydroxyl-bridge polymerization of Cr^{3+}. As the temperature continues to rise, the intensive evaporation of the plating solution decreases the stability. When the temperature is too low, the ion migration rate slows down and the cell voltage increases, which are not conducive to the electrodeposition reaction. The obtained coating surface is dark, and the edge part is attached with black oxide. With the increase of bath temperature, the overpotential of hydrogen evolution reduces, the cathode hydrogen evolution reaction intensifies, and the pH value near the cathode increases, facilitating the hydroxyl-bridge polymerization of Cr^{3+} and affecting the deposition of Cr^{3+}. Therefore, the temperature has a great influence on the Cr content of the high entropy alloy coating.

The SEM images in Fig. 7 present the morphologies of the FeCoNiCr alloy coatings deposited at different bath temperature T for 60 min. The XRD patterns for the FeCoNiCr alloy coatings are shown in Fig. 8. It can be seen from Fig. 7 that there are a few microcracks on the coating surface. When the bath temperature is 25 ℃, the grain size is fine and uniform, and the surface is relatively flat. With increasing the temperature, the grain size increases gradually, the cathode polarization decreases, the electrodeposition potential of FeCoNiCr high entropy alloy decreases, the particle growth accelerates, the nucleation rate decreases, the particle size increases, and the phase structure gradually becomes orderly. However, it is difficult to characterize this order. When the bath temperature is less than 20 ℃, the related reactions are not easy to occur, the solubility of main salt decreases, and the deposition rate of the coatings decreases, which are not conducive to the co-deposition of various ions on the surface of the substrate. Therefore, the FeCoNiCr high entropy alloy coatings cannot be obtained.

There is a broad diffraction peak near $2\theta=45°$ (Fig. 8), indicating an amorphous coating. With the increase of bath temperature, the Cr content of the coatings decreases gradually, and the Ni content increases rapidly, indicating that with the increase of bath temperature, the phase structure of the coatings gradually becomes ordered, and the copper peak gradually weakens until it disappears. This is because the deposition rate increases with increasing the bath temperature, and the coating thickness significantly increases. Therefore, the optimal bath temperature is 25 ℃.

2.3 Influence of pH on composition and hardness

The experiments were conducted under the condition of unchanged bath composition, bath temperature T=25 ℃, and current density D_K of 25 $A\cdot dm^{-2}$, and the influence of the pH value on the composition and hardness of coatings was studied. The electrodeposition time was set as 60 min. The results are shown in Fig.9 and 10, from which the optimal pH is obtained.

Fig.9 and 10 show the effect of different pH values on the composition and hardness of the coatings. When the pH value of the plating solution increases, the Cr content of the coatings decreases gradually, and the Ni content increases gradually.

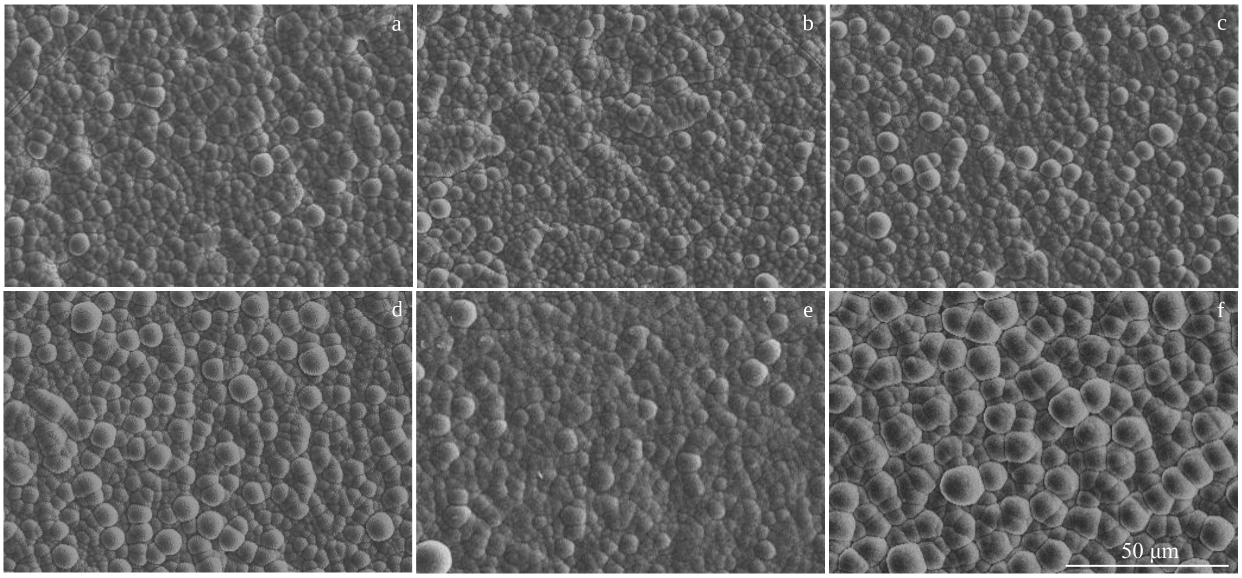

Fig.7 SEM images of FeCoNiCr coatings deposited at different bath temperatures T for 60 min: (a) 20 °C, (b) 25 °C, (c) 30 °C, (d) 40 °C, (e) 50 °C, and (f) 60 °C

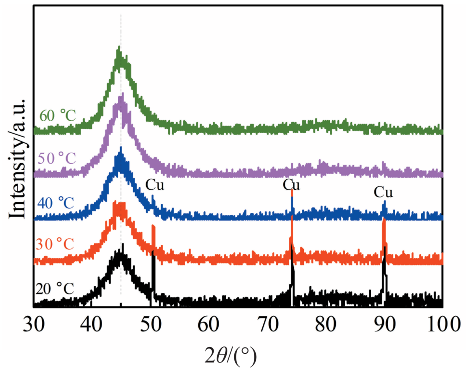

Fig.8 XRD patterns of FeCoNiCr alloy coatings deposited at different bath temperatures *T* for 60 min

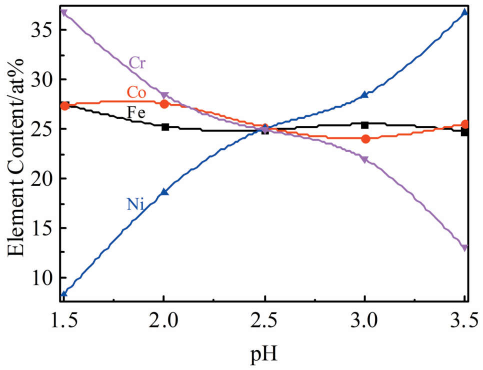

Fig.9 Relationship between element content in coatings and pH value

The hardness of the coatings increases at first and then decreases. When the pH value is 2.5, the content of each element of the coatings is approximately the same, and the hardness of the coatings reaches the maximum value. When the pH value is low, there are a lot of H^+ in the plating solution, which slows down the hydroxyl-bridge polymerization of Cr^{3+} and facilitates the electrodeposition process. The Cr content in the coatings is relatively high, but there are a lot of cracks and pores on the coating surface. So the hardness of the coatings is low. When pH>2.5, Cr forms a stable hydroxyl-bridge polymer and attaches to the cathode surface. So the Cr content of the coatings decreases, and the hardness also decreases.

The SEM images in Fig.11 present the morphologies of the FeCoNiCr alloy coatings deposited at different pH values for 60 min. The XRD patterns of the FeCoNiCr alloy coatings are shown in Fig.12.

With the pH value varies between 1.5~3.5, there are wide and blunt diffraction peaks near 2*θ*=45°. When the pH value is low, the side reaction of hydrogen evolution is violent, so the grain growth is uneven. In this case, there are many cracks

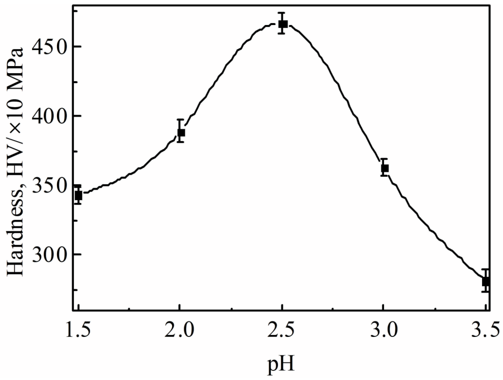

Fig.10 Relationship between hardness HV of coatings and pH value

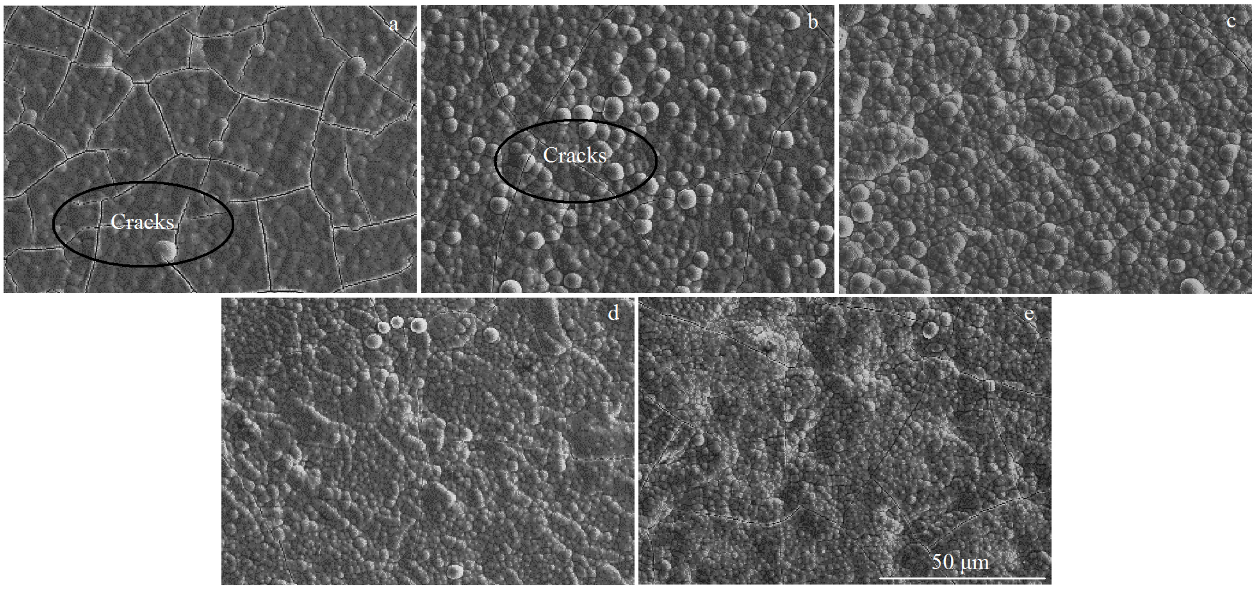

Fig.11 SEM images of FeCoNiCr coatings deposited at different pH values for 60 min: (a) pH=1.5, (b) pH=2.0, (c) pH=2.5, (d) pH=3.0, (e) pH=3.5

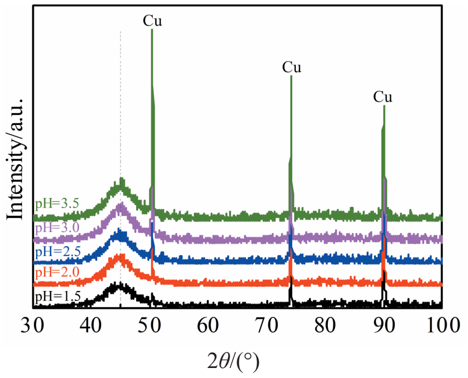

Fig.12 XRD patterns of FeCoNiCr alloy coatings deposited at different pH values for 60 min

and pores on the coating layer. With the increase of pH value, the reaction of hydrogen evolution slows down, thus the cracks on the coating surface decrease, and the pores disappear. When the pH value is 2.5, the coatings particles become uniform and fine, and the coating surface is bright. When the pH value continues to increase, the coating surface folds again and the number of cracks increases (Fig.11). When the pH value is too large, Cr^{3+} is beneficial to hydroxyl-bridge reaction, and a large amount of $Cr(H_2O)_3$ is generated on the cathode surface, reducing the coating quality. Therefore, the optimized pH value is 2.5.

Under the condition of D_K=25 A·dm^{-2}, pH=2.5, and T=25 °C, the obtained FeCoNiCr high entropy alloy coating is amorphous. The maximum hardness of the electrodeposited coating is above 6000 MPa, which is higher than that of the AlCoNiFeCr high entropy alloy coating prepared by mechanical alloying (5900 MPa)[11].

3 Conclusions

1) The optimal electrodeposition system for preparation of FeCoNiCr high entropy alloy coatings is obtained. The optimal process parameters are: current density D_K of 25 A·dm^{-2}, pH value of 2.5, and bath temperature T of 25 °C.

2) The Cr content and hardness of the coatings increase with increasing the current density D_K.

3) With the increase of bath temperature, the Cr content decreases, while the Ni content, grain size, and the hardness of coatings increase. However, when the temperature is too high, the hydroxyl-bridge polymerization reaction occurs due to Cr^{3+}, and the cracks appear on the surface.

4) With the increase of the pH value, the Cr content and the hardness of the coatings increase at first and then decrease. When the pH value is 2.5, the hardness of coating is the highest, and the coatings quality is the best.

References

1 Tu Zhenmi, An Maozhong, Hu Huili. *Theory and Technology of Modern Alloy Electrodeposition*[M]. Beijing: National Defense Industry Press, 2016: 25 (in Chinese)
2 Yeh J W, Chen S K, Lin S J *et al. Advanced Engineering Materials*[J], 2004, 6(5): 299
3 Xu Jun, Cao Chengming, Gu Ping *et al. Transactions of Nonferrous Metals Society of China*[J], 2020, 30(3): 746
4 Yeh J W, Chen S K, Gan J Y *et al. Metallurgical and Materials Transactions A*[J], 2004, 35(8): 2533
5 Liu L, Zhu J B, Zhang C *et al. Materials Science and Engineering A*[J], 2012, 548: 64
6 Li Jinshan, Jia Wenjuan, Wang Jun *et al. Materials & Design*[J], 2016, 95: 183
7 Zhang C, Gao M C, Lin S K. *JOM*[J], 2019, 71(10): 3417
8 Miracle D B, Senkov O N. *Acta Materialia*[J], 2017, 122: 448
9 Zhang W R, Liaw P K, Zhang Y. *Science China Materials*[J], 2018, 61(1): 2
10 Wang Jun, Guo Tong, Li Jinshan *et al. Materials Chemistry and Physics*[J], 2018, 210: 192
11 Jiang Ye, Chen Ke, Wang Wei. *The Chinese Journal of Nonferrous Metals*[J], 2018, 28(9): 1784 (in Chinese)
12 Zhao Haichao, Liang Xiubing, Qiao Yulin *et al. Journal of Materials Engineering*[J], 2019, 47(10): 33 (in Chinese)
13 Zhang Yong. *Amorphous and High Entropy Alloys*[M]. Beijing: Science Press, 2010: 18 (in Chinese)
14 Feng Shaobin, Feng Liting, Shang Shibo. *Materials Protection*[J], 2004, 37(1): 46 (in Chinese)
15 Xu Lijian, Gong Zhuqing, Yang Yufang *et al. Electroplating & Finishing*[J], 2006, 25(4): 8 (in Chinese)
16 Shang Hongwu, An Maozhong, Yang Peixia *et al. Electroplating & Pollution Control*[J], 2009, 29(1): 5 (in Chinese)

FeCoNiCr高熵合金涂层的制备及工艺参数优化

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摘 要：以柠檬酸和柠檬酸钠为络合剂，采用硫酸盐体系电沉积法制备了FeCoNiCr高熵合金镀层。研究了电流密度、镀液温度、pH对镀层组成、微观形貌、晶体结构和硬度的影响。结果表明，所制备的FeCoNiCr高熵合金镀层为非晶态，镀层均匀。优化后工艺参数为：pH=2.5，温度25 ℃，电流密度25 A·dm^{-2}。

关键词：FeCoNiCr高熵合金；电沉积；形貌；晶体结构；硬度

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