Deposition Technology and Microhardness of Electrochemical Deposited Ni-W Alloy Nanocrystalline

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Abstract : In this paper, a perpendicular experiment was conducted by using 4 key process parameters, such as concentration of sodium tungstate, current density, PH value and operating temperature, which have obvious influence on the electrodeposition of Ni-W alloy nanocrystalline. By extreme difference analysis, the influence of multi-factors on the deposition rate and microhardness and surface quality of the nanocrystalline alloy coatings was studied in detail. By further contrastive experiment, the influence of single-factor on the electrodeposition of Ni-W alloy nanocrystalline was also discussed, which will provide basis for the preparation of Ni-W alloy nanocrystalline.

Key word: Ni-W alloy, electrodeposition, nanocrystalline

ELECTRODEPOSITED Ni-W alloy has potential to substitute hard chromium in many applications because of high hardness and excellent corrosion and wear resistance. At present, There are many studies concerning about the influence of single factor on the composition and the structure of the coatings, but the studies about the influence multi-factors have not been reported. At the same time, electrodeposition is one of the most potential ways to prepare entirely compact nanocrystalline [1-2]. One can obtain nanocrystalline by controlling process conditions, such as temperature, PH value, current density, the area of anode and cathode, and the distance from anode to cathode [3-4].

In this paper, a perpendicular experiment was conducted by using 4 key process parameters, such as concentration of sodium tungsten, current density, PH value and operating temperature, which have greater influence on the electrodeposition of Ni-W alloy nanocrystalline, the influence of multi-factors on the deposition rate and micro hardness and surface quality of the nanocrystalline alloy coating was studied. By further contrastive experiment, the influence of single-factor on the electrodeposition of Ni-W alloy nanocrystalline was also discussed, which will provide reference for the preparation of Ni-W alloy nanocrystalline.

1. Experimental

The composition of the bath was recommended as below: $NiSO_4.6H_2O$ 15g/l, $Na_2WO_4{\cdot}2H_2O$ 10, 20, 30, 40, 50g/l, $C_6H_8O_7{\cdot}H_2O$ 40~70g/l, a coating bath was made using analytical reagent and distilled water. pH value was adjusted using ammonia.

(1) Bath preparation: The required reagents were weighed respectively, and soluted them in the distilled water. Added the $Na_2WO_4{\cdot}2H_2O$ solution into the $NiSO_4{\cdot}6H_2O$ solution and agitated the mixture solution completely, we can observe the formation of a precipitant. The citric acid solution was put into the solution and agitated it completely until the precipitant gradually dissolved, then filtered the solution and added the ammonia into it to adjust the PH value. Using the précised test paper to check the PH value, finally added the distilled water to the prescriptive volume. Water bath was used to heat the beaker that contained the bath to the operated temperature.

(2) Codeposition devices: pure nickel plate was used as the anode and the mild steel plate (3.0×2.0 cm^2 in size)×2 sides were used as the cathode. The codeposited operation and parameters control was performed using HHS electro thermal homothermal water bath and Qingyan-2 type hull bath test apparatus.

(3) Characterization: TG528B damp analytical balance, Shanghai-71 micro hardness tester (load was 100g, keeping 15s), XJL-02 Jiang Nan optical upright metallographic microscope, D/max-γB X-ray diffractor (graphite monochromator, Cu K_α radiation, tube voltage was 40 kv, tube current was 80mA, scanning speed was 6°/min.) were used to monitor the deposition Cand haracterize the composite coatings.

2. Results and Discussion

2.1 Influence of the Concentration of Sodium Tungstate on the Depositing Rate and Hardness

In order to further study influence of the processing parameters on the electrodeposition of Ni-W alloy nanocrystalline, each factor effects were evaluated.

As shown in Fig.1 and Fig.2, the electrodeposition rate of Ni-W alloy generally decreased with the increasing of the concentration of sodium tungstate when the concentration of sodium tungsten was 30 g/l, the microhardness attained the highest value that was up to H_V 647.4.

It was found that the microhardness would be rise with the increase of the tungsten content. When the tungsten content rose, lattice distortion would increase, the resistance of moving dislocation would increase [6], then the microhardness of alloy samples would increase.

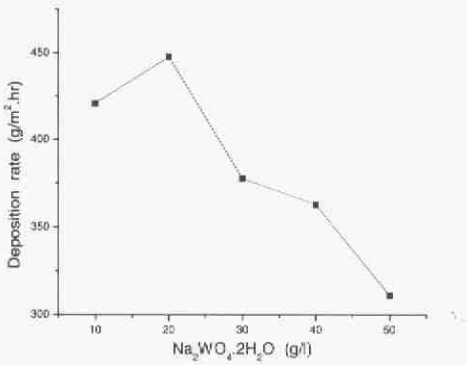


Fig.1 Influence of the concentration of sodium tungstate on the depositing rate

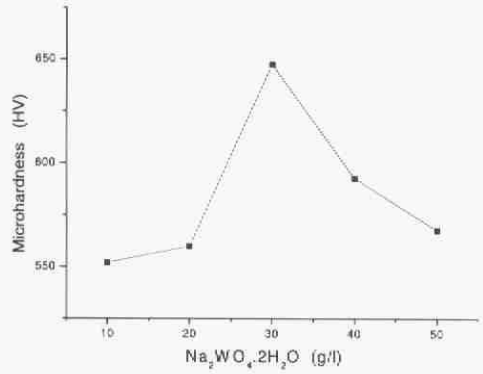


Fig.2 Influence of the concentration of sodium tungstate on the microhardness

The samples denoted as No.1-5 were analyzed by X-ray diffraction (the concentration of sodium tungstate was respectively 10, 20, 30, 40, 50g/l) as shown in Fig.3. Three X-ray diffraction peaks in No .1 sample emerged (diffraction angles: $2\theta_1$=43.86°, $2\theta_2$=51.28°, $2\theta_3$=75.6°). It can be determined as the crystalline coating. Three most highest peak position of pure nickel was respectively coincident to $2\theta_1$=44.62°, $2\theta_2$=51.94°, $2\theta_3$=76.14°. However, the three most highest peak positions of pure tungsten were $2\theta_1$=40.26°, $2\theta_2$=58.36°, $2\theta_3$=73.38° respectively. We can find that the peak position of Ni-W alloy was extremely close to the peak position of pure Ni. It was ascertained that the Ni-W alloy was displacing solid solution with the solvent of nickel and the solute of tungsten [7]. The atomic radius of nickel is 1.20Å and the atomic radius of tungsten is 1.37Å, when nickel and tungsten form solid solution the partial lattice distortion generated, and the lattice constant of the coating increased based on Bragger formula $2d\sin\theta=n\lambda$, when d value increases θ value will decrease, so 2θ angle should move to the low angle direction that is corresponding to the experimental results.

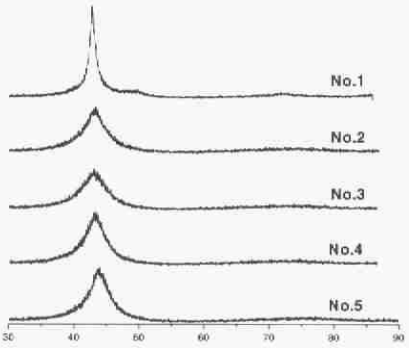


Fig.3 XRD of electrodeposited Ni-W alloy coatings

According to Scherrer formula $L=k\lambda/\beta\cos\theta$, the grain size can be calculated in the formula. L: grain mean size; K: constant, is generally 0.89; λ: the wavelength of x-ray, λ=0.15406nm (Cu kα radiation), β: the peak half width of x-ray; θ: the half of diffraction angle 2θ. By calculation, the grain mean size of No.1 sample was about 30.2 nm, the x-ray diffraction peak of No.2、3、4、5 samples would be widened and stunt, and only an obvious diffraction peak emerged. Its microstructure could be depicted in the state between amorphous state and crystalline state. The grain size was very small. The peak of No.3 sample was widest and lowest and it trended to preferred orientation. The average atomic distances in the coatings of No.2～5 samples were 17.66～25.68nm which were estimated by scherrer formula. The widened extent of x-ray diffraction showed the dissolution of tungsten caused inhomogeneous lattice distortion and the lattice distortion would increase with the rising of the content of tungsten, and the long-range order of the alloy would be destroyed. The orientation of the grains tended to the transformation of the short-range order. Namely the samples with the same [hkl] owned different d value indifferent small areas, d value varied in the range of $d_{hkl}\pm\triangle d$, $\triangle d$ was small, but was not a constant. So the diffraction angle position of the same crystal indices would deviate, finally it composed a broadening peak with a certain of density in the range of $2\theta\pm\triangle\theta$. The microhardness of No.3 sample was most highest and its tungsten content was also highest. This was corresponding to the character of the XRD figure of No.3 sample.A large number of studies [4] [7-10] show that when the content of tungsten is up to 44%(wt), the structure of the alloy coating will change into the amorphous structure with the short-range order rather than the long-range disorder, leading to many excellent properties, such as corrosion resistance and wear resistance etc.

2.2 Influence of the pH Value on the Depositing Rate and Microhardness

As shown in Figure 4, 5, ($Na_2WO_4\cdot2H_2O$ was 30 g/l, T=80 °C, D_k=15A/dm^2, t=60min), when pH value was

in the range from 6 to 8, the microhardness eached to more than HV 600, the deposited rate would increase with increasing of the pH value. When pH value was more than 7, the depositing rate increased rapidly. The surface quality of the coatings was depending strongly on pH value. When pH value was in the range from 5 to 7, we can obtain the bright & delicate coating. However, as pH value got to 7, the surface of the samples changed into the dim color, and pH value attaining to 10 would result in the higher depositing rate. The coatings roughened and the microhardness would decrease. When pH value was low, separating hydrogenreaction was violent and hydrogen provided more centers for crystallizing nucleation for Ni-W alloy during the reduction process, so the coating crystallized delicately, and the grains were refined. Through the metallographic microscope analysis, the surface of the coatings grew in the form of granulated particles, the granulated morphology obtained in the alkali solution was especially representative. The surface morphology of the coatings obtained during different depositing conditions are shown in Fig. 6

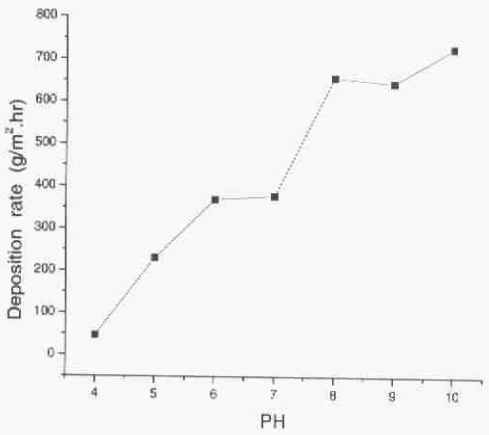


Fig. 4 Changes of deposited rate with pH value

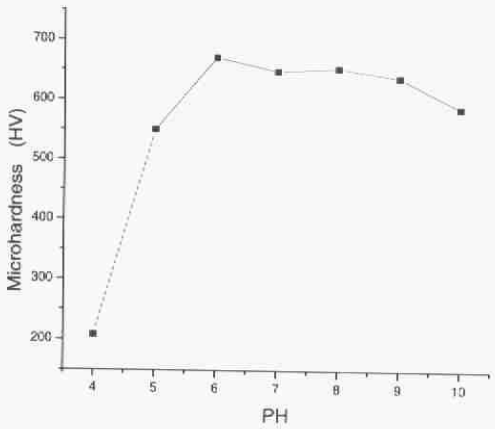
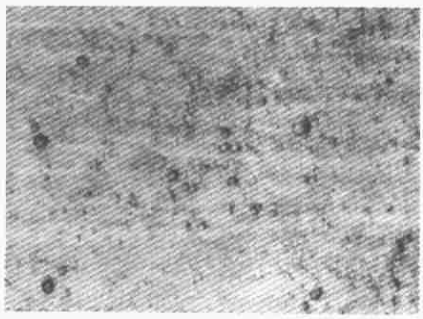
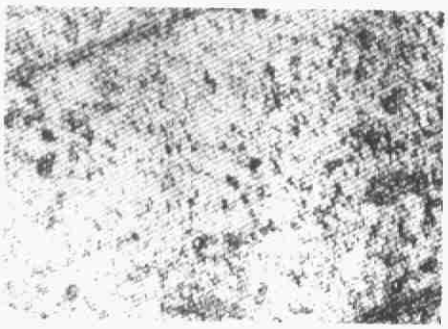


Fig. 5 Changes of microhardness with pH value

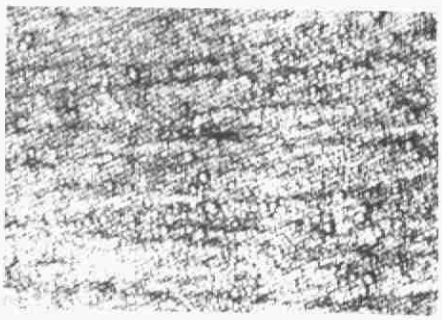


(a) Na2WO4.2H2O 30g/l, T=80℃, DK =15A/dm2, pH =7, t=60min

(b) Na2WO4.2H2O 40g/l, T=80℃, DK =15A/dm2, pH =7, t=60min



(c) Na2WO4.2H2O 50g/l, T=80℃, DK =15A/dm2pH =7, t=60min



(d) Na2WO4.2H2O 30g/l, T=80℃, DK =15A/dm2, pH =9, t=60min

Fig. 6 Surface morphology of electrodeposited Ni-W alloy coatings

2.3 Influence of the Current Density on the Depositing Rate and Microhardness

The Influence of the current density on the depositing rate and hardness was shown in Fig.7,8

($Na_2WO_4 \cdot 2H_2O$ 30g/l, PH=7, T=80℃, t=60min). With the increase of D_k, the deposited rate and microhardness increased. As D_k was 15A/dm^2, the quality of the surface is the best, and the microhardness is the highest. D_k attained to 20 A/dm^2, the numerical value of microhardness was up to HV646.8 but the surface of the sample occurred the crack and the edge had crusting. So when deposition rate was too high, the adhesion of the coating with substrate was degenerated with high internal stress. The reason was that with the increase of D_k, the increase of over potential on the pole was beneficial to the form of the crystal nucleus in the processing of electrodeposition of Ni-W alloy. But the nuclear grown is restricted relatively. So the size of the crystal decreased and microhardness increased. However, when D_k was too high, deposition ion consumed near cathode in the electrolyte wouldn't complement in time. So the quantity of the coating decreased.

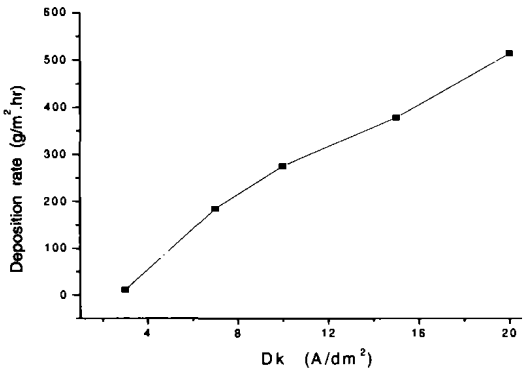


Fig. 7 Changes of depositing rate with Dk

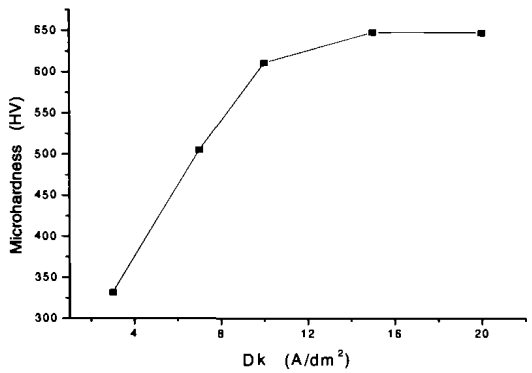


Fig. 8 Changes of microhardness with Dk

3. Conclusion

(1) The deposition rate, microhardness and appearance of the electrodeposited Ni-W nanocrystalline alloy coatings were depending strongly on PH value, the suitable bath was neutral or acescent.

(2) The current density also had remarkable effect on the electrodeposited Ni-W nanocrystalline alloy. With the current density, the deposition rate and microhardness all increased. However, when D_k was 20A/dm^2, the surface quality of the coating was decreased, so D_k in the range from 10 to 20 A/dm^2 was suitable.

(3)The mean grain size of the crystalline coating obtained in this experiment was about 30.2nm.

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