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Short Communication

Effect of Laser Heat Treatment on Mechanical Property of NiW/Ni Coating Electrodeposited on Copper Substrate

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In this paper, NiW/Ni duplex coating is electrodeposited on the surface of copper substrate. The laser heat treatment technology is used to greatly improve the mechanical property of NiW/Ni duplex coating. The electrodeposition of NiW belongs to induced codeposition. NiW is a kind of alloys with tungsten as solute and nickel as solvent that belongs to the face-centered cubic structure with granular morphology. Tungsten doped into the crystal lattice of nickel can effectively refine grain size. The laser beam has high energy density, and the instantaneous high temperature can reduce the residual stress and improve the hardness of the coating. Moreover, the coating is cooled quickly after laser scanning, which helps to refine the grain size. The NiW/Ni duplex coating after laser heat treatment has the best hardness and optimal mechanical property.

Keywords: Electrodeposition; NiW/Ni duplex coating; Laser heat treatment; Mechanical property;

1. INTRODUCTION

Copper has many excellent physical and chemical properties, such as high thermal conductivity, strong chemical stability, good corrosion resistance and so on. Therefore, copper material is widely used in power transmission, mechanical and electrical manufacturing, mechanical equipment and other fields [1-5]. However, the hardness and wear resistance of copper is not good enough that limits its application. It is found that the mechanical properties of copper can be improved effectively by preparing nickel or nickel alloy on the surface of copper. Some nickel-based alloy coatings have excellent physical and chemical property reported in many literatures, such as NiW, NiZn, NiP, NiMo and so on [6-10]. The nickel coating itself has excellent corrosion resistance and better wear resistance. By doping tungsten, molybdenum, phosphorus and other elements in the nickel coating, nickel-based alloy can be formed, which greatly improves the mechanical properties. At present, many methods can be used to prepare nickel-based alloys on copper, such as magnetron sputtering, ion beam epitaxy, chemical vapor deposition, electrodeposition and so on. Among them, electrodeposition method has attracted the interest of many researchers due to its advantages of simple equipment, low cost and easy implementation. Many scholars have prepared Ni-based alloy coatings on copper by electrodeposition so far [11-14].

Moreover, it is also found that heat treatment can be used to refine the grain size of metal alloy coating to further improve its property [15-17]. With the rapid development of laser technology, laser heat treatment becomes a very innovative technology. By irradiating the metal surface with a laser, the temperature of the metal surface can be raised rapidly. After the laser beam is removed, the metal surface can be cooled rapidly. Laser heat treatment has significant effect on wear resistance, corrosion resistance, fatigue resistance and impact resistance of metal surface [18-20]. Moreover, the advantages of laser heat treatment are no pollution and strong controllability which has broad application prospects. Therefore, NiW/Ni duplex coating is prepared on the surface of copper substrate in the paper. The effect of laser heat treatment on the surface morphology, roughness, structure, hardness, wear resistance of coatings is investigated.

2. EXPERIMENTAL

2.1 Materials and chemical agents

The detail information about the chemical agents used in the experiment is as follows: $C_6H_8O_7$, Na_2WO_4, $NiSO_4$, H_3BO_3 and Na_2SO_4. All the chemical agents are chemical pure. The plating solution is 100 ml with pH=6 and the plating time is 1 hour at the current density of 2.5 A/dm^2 and the temperature of 30 ℃.

The pure copper with exposed area (2 cm×4 cm) is as the cathode and the pure platinum with exposed area (4 cm×4 cm) is as the anode. The pure copper is polished firstly by a polish machine. And then, the copper substrate is immersed into the alkali solution (30 g/L NaOH) for 5 mins at 60 ℃ to remove oil. After being cleaned by pure water, the copper substrate is immersed into the acid solution (10% HCl) to get rid of rust. Finally, the copper substrate is cleaned and dried to do the electrodepostion.

2.2 Experimental process of NiW/Ni duplex coating

Firstly, the Ni coating on copper is prepared from the 100 ml plating solution (0.3 mol/L $C_6H_8O_7$, 0.05 mol/L $NiSO_4$, 0.5 mol/L H_3BO_3, 0.1 mol/L Na_2SO_4) at the condition of 2.5 A/dm^2 and 30 ℃ for 1 hour.

Secondly, The Ni coating on copper is immersed into the other 100 ml plating solution (0.3 mol/L $C_6H_8O_7$, 0.05 mol/L Na_2WO_4, 0.05 mol/L $NiSO_4$, 0.5 mol/L H_3BO_3, 0.1 mol/L Na_2SO_4) as the cathode to obtain NiW/Ni duplex coating on copper at the condition of 2.5 A/dm^2 and 30 ℃ for 1 hour.

Finally, the NiW/Ni duplex coating on copper is treated by laser heat treatment. The coating is placed on the sample table, and a laser generator (NEL2500) is used to generate laser and irradiate the sample surface. The laser power is 500 W and the scanning rate is 1 mm/s.

2.3 Testing method

The cathodic polarization curve of copper in different plating solutions is tested by electrochemical station (CHI760E) from 0 V to -1.5 V at the scan rate of 5 mV/s. The copper of 1 cm×1 cm size is the working electrode and the pure platinum of 4 cm×4 cm size is the counter electrode. Saturated calomel electrode is as the reference electrode. The roughness of coatings is tested by surface profiler (CV3200). The scanning length is 2000 μm at the scanning rate of 10 μm/s. The surface morphology and structure of coatings are characterized by scanning electron microscope (TM4000PLUS) and X-ray Diffraction (PW1700) respectively. The scanning range is from 20° to 100° with the scanning rate of 4°/min. The Vickers hardness tester (HV-1000Z) is used to test the surface hardness of coatings. The loading force is 100 g at 15 s holding time. The mechanical property of coatings is evaluated by scratch meter (MFT4000). The loading force is from 0 to 40 N at 1 min.

3. RESTULS AND DISCUSSION

3.1 Cathode polarization curves of copper in different plating solutions

The cathode polarization curve of copper in different plating solutions can be seen in the Figure 1. Regarding to Figure 1(a), the cathode current of plating solution with 0.05 mol/L Na_2WO_4 starts to increase slowly at the position (b_1) of -1.4 V. Tungsten has a very negative precipitation potential, so it is generally difficult to obtain tungsten from an aqueous solution. Some people found that tungsten can be electrodeposited from molten salts [21-23]. According to Figure 1(b), the cathode current of solution with nickel ions increase extremely at the position (a_1) of -0.881 V which demonstrates that the nickel precipitation is dominant at this position. However, the cathode current of solution containing both nickel ions and tungstate ions begins to increases obviously at the potential of -0.977 V (c_1) which is between a_1 and b_1. It can be found that compared with nickel, NiW alloy electrodeposition requires more negative deposition potential. The addition of tungstate ions in the solution hinders the deposition of nickel to a certain extent. When the citric acid is added in the solution, the obvious precipitation potential of NiW moves more negative to -1.03 V (d_1). The addition of complexing agent in electrodeposition solution will make the deposition potential of metal shift negatively [24-26]. Codeposition of nickel and tungsten is called induced codeposition. It is generally believed that the complex of nickel and tungsten will be formed under the complexation of citric acid, and this complex will be deposited to form NiW alloys which can be explained by equations below [27].

$$NiCit^{-} + 2e^{-} \rightarrow Ni + Cit^{3-} \qquad (1)$$

$$WO_4^{2-} + 2H_2O + 2e^- \xrightarrow{NiCit^-} WO_2 + 4OH^- \quad (2)$$

$$WO_2(2H_2O) + 4H(Ni) \rightarrow Ni(W) + 2H_2O \quad (3)$$

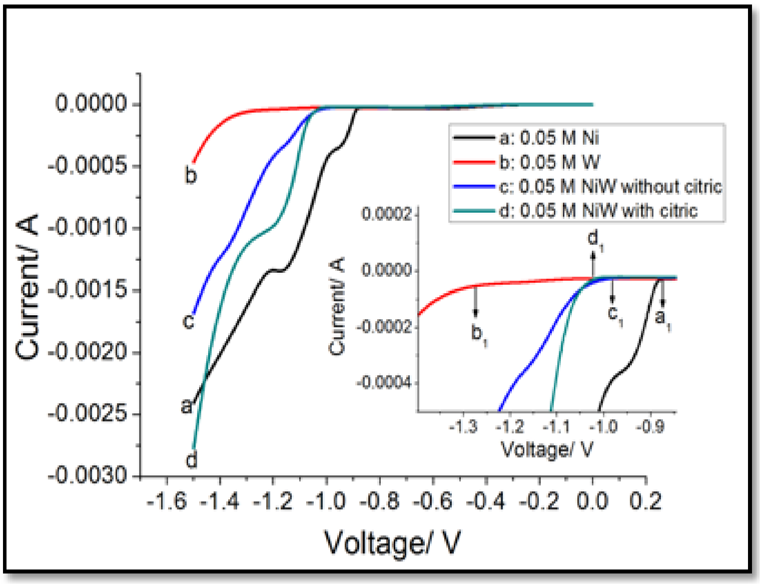

Figure 1. The cathodic polarization curve of copper in different plating solutions; a: 0.05 mol/L $NiSO_4$; b: 0.05 mol/L Na_2WO_4; c: 0.05 mol/L $NiSO_4$+0.05 mol/L Na_2WO_4; d: 0.05 mol/L $NiSO_4$+0.05 mol/L Na_2WO_4+0.3 mol/L citric acid; The copper of 1 cm×1 cm size is the working electrode and the pure platinum of 4 cm×4 cm size is the counter electrode. Saturated calomel electrode is as the reference electrode. The scan rate is 5 mV/s.

3.2 Surface morphology and structure of NiW/Ni duplex coating

Scanning electron microscopy is used to observe the surface morphology of NiW/Ni duplex coating, and the results are shown in Figure 2. As can be seen from the surface morphology of Figure 2, the prepared Ni coating and NiW/Ni duplex coatings both show typical granular morphology which are also reported by some people [28-29]. The surface particles of Ni coating are larger and agglomeration is obvious. Compared with Ni coating, NiW/Ni duplex coating has uniform and compact surface composed of much smaller particles.

The electrodeposition of the nickel and tungsten belongs to induced codeposition, tungsten doped into the crystal lattice of nickel can effectively refine grain size. After laser heat treatment, it is found that the particles on coating surface are further refined. In addition, a small amount of black products with larger roughness can be observed. Some oxides are generated on the surface of the coating due to high heat produced by laser. The laser beam has high energy density, and the instantaneous high temperature can improve the bonding strength of the substrate and coating. Moreover, the coating is cooled quickly after laser scanning, which helps to refine the grain size.

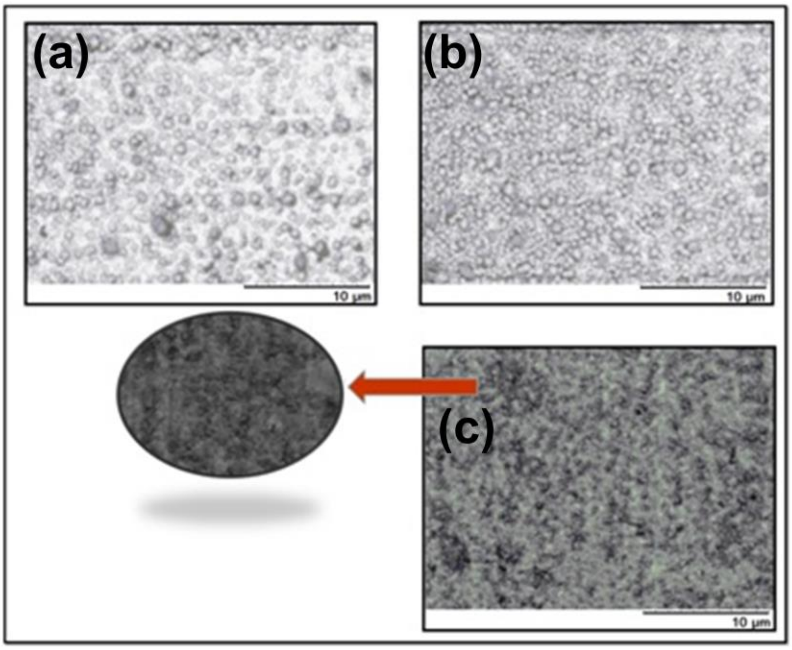

Figure 2. Surface morphology of Ni coating, NiW/Ni duplex coating and NiW/Ni duplex coating after laser heat treatment; (a) Ni coating; (b) NiW/Ni duplex coating; (c) NiW/Ni duplex coating after laser heat treatment.

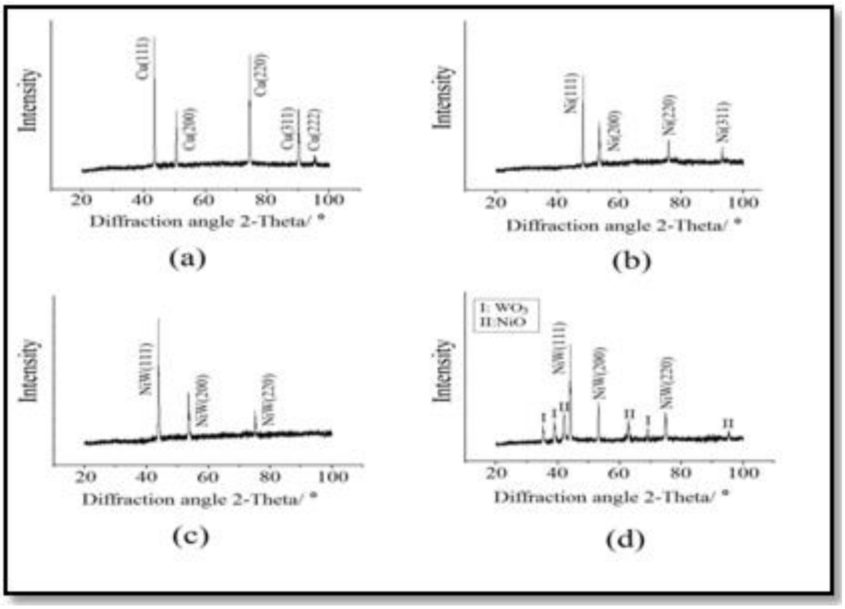

Figure 3. XRD patterns of Cu, Ni coating, NiW/Ni duplex coating and NiW/Ni duplex coating after laser heat treatment; The scanning angle is from 20° to 100° with 4°/s scanning rate; (a) copper substrate; (b) Ni coating; (c) NiW/Ni duplex coating; (d) NiW/Ni duplex coating after laser heat treatment;

The XRD patters of Cu, Ni coating, NiW/Ni duplex coating and NiW/Ni duplex coating after laser heat treatment are shown in Figure 3. According to Figure 3(a), the typical diffraction peaks of copper could be observed at the position of 2θ=43.2°, 2θ=50.4°, 2θ=73.1° and 2θ=89.2° respectively. The four strong diffraction peaks of nickel locate at 2θ=44.5°, 2θ=51.9°, 2θ=76.5° and 2θ=92.9°

respectively which indicate the cubic structure. The crystallinity of NiW/Ni duplex coating obtained by electrodeposition is good, and three strong diffraction peaks appear on the crystal plane NiW(111), NiW(200) and NiW(220), respectively. Nickel belongs to face-centered cubic structure and tungsten belongs to body-centered cubic structure. NiW is a kind of alloy with tungsten as solute and nickel as solvent and belongs to the face-centered cubic structure, in which tungsten atoms occupy the lattice of nickel atoms. Some researchers also report and prepare NiW alloy with same structure [30-31]. After laser heat treatment, the diffraction peak intensity of NiW decreases and the peak width increases, indicating that the grain of the alloy is refined. In addition, in addition to the three diffraction peaks of NiW alloys, some miscellaneous peaks can be observed, mainly corresponding to the oxides of nickel and tungsten.

Roughness of samples is listed in both Figure 3 and Table 1. Meanwhile, Ra is arithmetic mean value of absolute offset of contour in sampling length. R_z is the distance between the peak and the valley. R_p is the maximum peak within the sampling length. According to the Table 1, the roughness of copper substrate is round 0.526 μm. The roughness of Ni coating is about 0.237 μm while the roughness of NiW/Ni duplex coating is approximate 0.193 μm. However, after laser heat treatment, the roughness of NiW/Ni duplex coating increases, mainly due to the formation of a small amount of tungsten and nickel oxides on the surface during laser heat treatment, which increases the roughness of the surface.

Table 1. Ra, R_z and R_p of Cu, Ni coating, NiW/Ni duplex coating and NiW/Ni duplex coating after laser heat treatment

Sample	R_a / μm	R_z / μm	R_p / μm
Copper	0.526	4.143	2.242
Ni coating	0.237	1.972	0.701
NiW/Ni duplex coating	0.193	1.273	0.431
NiW/Ni duplex coating after laser heat treatment	0.629	7.32	5.01

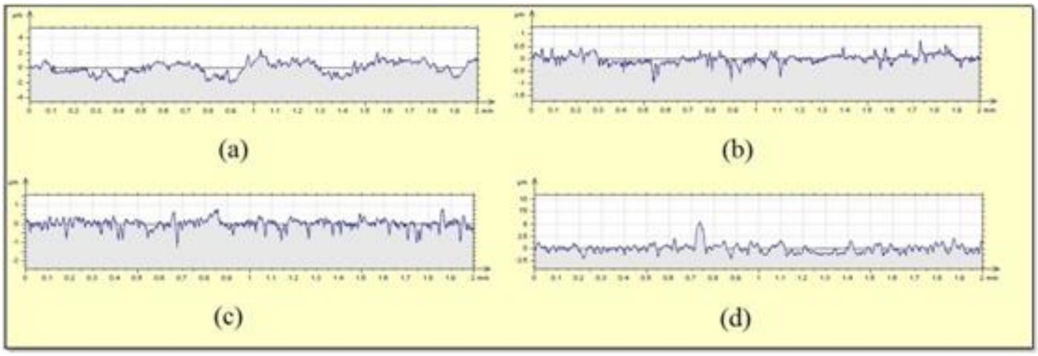

Figure 4. Roughness of Cu, Ni coating, NiW/Ni duplex coating and NiW/Ni duplex coating after laser heat treatment; The scanning range is from 0 μm to 2000 μm at the scanning rate of 10 μm/s; (a) copper substrate; (b) Ni coating; (c) NiW/Ni duplex coating; (d) NiW/Ni duplex coating after laser heat treatment;

3.3 Hardness and mechanical property of NiW/Ni duplex coating

The hardness of different samples are tested and shown in Figure 5. It can be seen that the hardness of copper substrate is around 90 HV while the hardness of Ni coating is approximate 120 HV. However, hardness of NiW/Ni duplex coating is up to 550 HV which is almost six times larger than that of copper substrate.

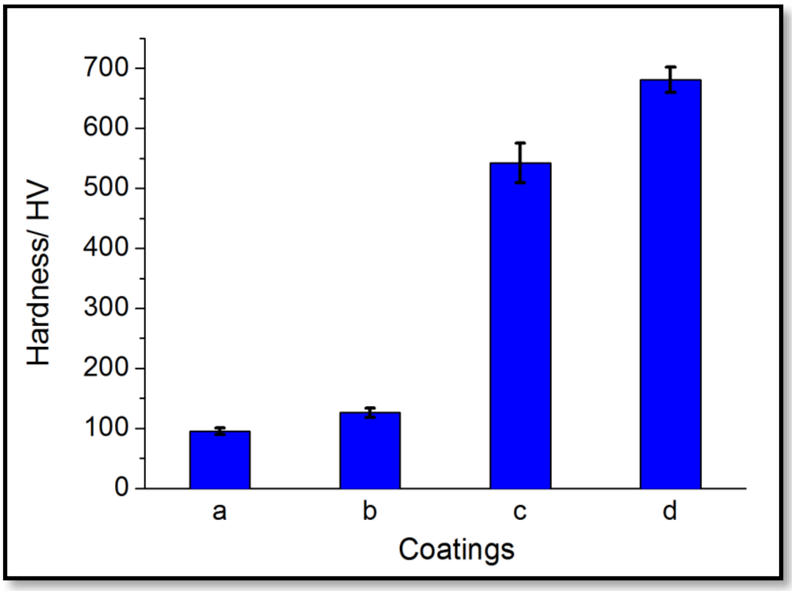

Figure 5. Hardness of Cu, Ni coating, NiW/Ni duplex coating and NiW/Ni duplex coating after laser heat treatment; The loading force is 100 N with holding time 15 s; (a) copper substrate; (b) Ni coating; (c) NiW/Ni duplex coating; (d) NiW/Ni duplex coating after laser heat treatment;

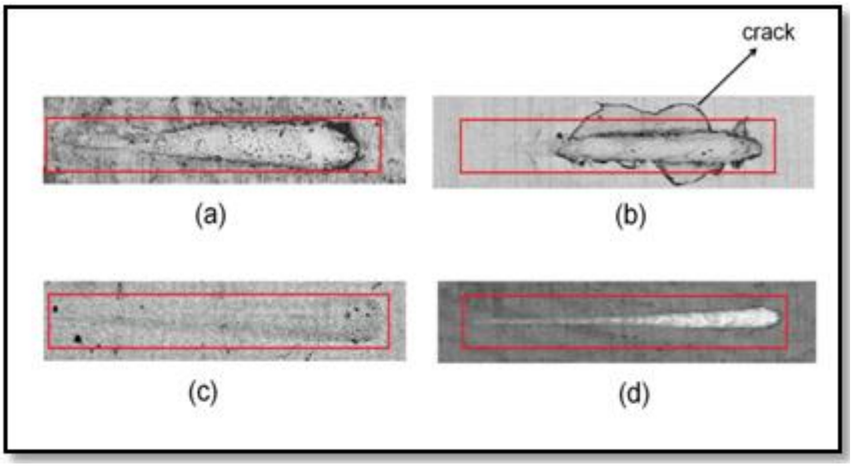

Figure 6. Scratch morphology of Cu, Ni coating, NiW/Ni duplex coating and NiW/Ni duplex coating after laser heat treatment; The loading force is from 0 N to 40 N to produce 3 mm length scratch; (a) copper substrate; (b) Ni coating; (c) NiW/Ni duplex coating; (d) NiW/Ni duplex coating after laser heat treatment;

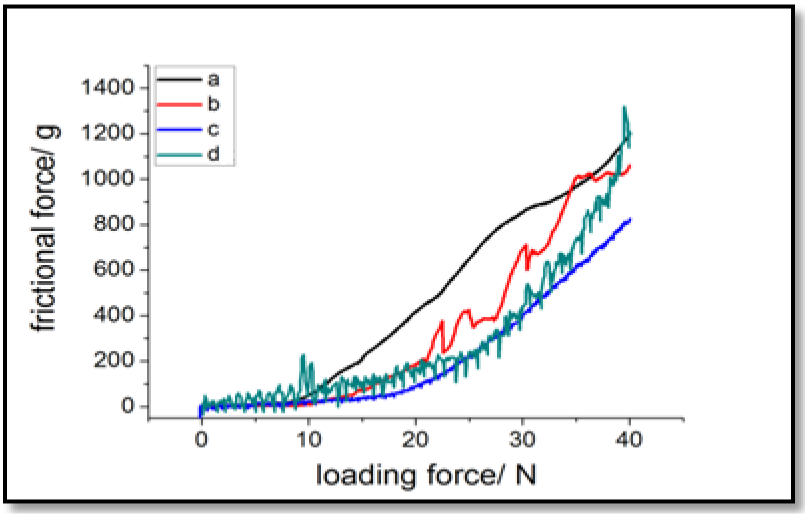

Figure 7. Frictional force of Cu, Ni coating, NiW/Ni duplex coating and NiW/Ni duplex coating after laser heat treatment; The loading force is from 0 N to 40 N; (a) copper substrate; (b) Ni coating; (c) NiW/Ni duplex coating; (d) NiW/Ni duplex coating after laser heat treatment;

As can be seen from the previous analysis, NiW electrodeposited belongs to the face-centered cubic structure, in which tungsten atoms occupy the lattice of nickel atoms to decrease grain size and form compact surface resulting in the increase of hardness. After laser heat treatment, the hardness of NiW/Ni duplex coating is greatly improved, reaching 700 HV. On the one hand, instant high temperature produced by laser can reduce the residual stress of the coating and improve the hardness of the coating. On the other hand, the instant cooling after laser beam is removed can not only refine the grain structure of the coating, but also improve the compactness of the coating, thus greatly improving the hardness of the coating.

The mechanical properties of the samples are tested with a scratch meter, and the results are shown in Figure 6 and Figure 7. As the load gradually increases from 0 N to 40 N, the friction force of the sample also increases simultaneously. Compared with other samples, the NiW/Ni duplex coating has the lowest surface roughness and the smallest friction force. After laser heat treatment, a small amount of oxidation products on the surface of the coating increases the roughness of the coating and makes the friction increase. The mechanical properties of the coating can be evaluated according to the scratch morphology in Figure 6. Copper has the widest surface scratch because of its lower hardness. According to Figure 6(b), the surface scratch of the Ni coating is thinner than that of the copper coating, but some cracks can be observed on the surface of the Ni coating. The scratch on the surface of NiW/Ni duplex coating is thinner than that on the surface of Ni coating, indicating that the mechanical property of NiW/Ni duplex coating is better. After laser heat treatment, NiW/Ni duplex coating has the smallest scratch morphology and excellent mechanical properties. Analysis shows that laser treatment can not only refine the grain structure of the material, but also improve the compactness, reduce or eliminate the micro-cracks in the coating, thus improving the mechanical properties [32-34].

3. CONCLUSIONS

NiW/Ni duplex coating is electrodeposited on the surface of copper and laser heat treatment is used to improve the mechanical property of NiW/Ni duplex electrodeposited coating. The surface morphology, roughness, structure and mechanical property of NiW/Ni duplex coating are investigated. The prepared Ni coating and NiW/Ni duplex coating both show typical granular morphology. The electrodeposition of the nickel and tungsten belongs to induced codeposition, tungsten doped into the crystal lattice of nickel can effectively refine grain size. The crystallinity of NiW/Ni duplex coating obtained by electrodeposition is good, and three strong diffraction peaks appear on the crystal plane NiW(111), NiW(200) and NiW(220), respectively. Instant high temperature produced by laser can reduce the residual stress of the coating and improve the hardness of the coating. Moreover, the instant cooling after laser treatment is removed can not only refine the grain structure of the coating, but also improve the compactness of the coating, thus greatly improving the hardness of the coating. After laser heat treatment, the hardness and mechanical property of NiW/Ni duplex coating both increase sharply.

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