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Effect of Ni-W microcrystalline coating on plastic deformation behavior of Cu substrate

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Abstract

Microcrystalline Ni-W alloy layers with different thickness were electroplated on the surface of Cu substrate. The mechanical properties of coating samples with different thickness were analyzed. The microstructure and fracture morphology between the substrate and the coating were observed by SEM (scanning electron microscopy) and EDS (energy dispersion spectrum). The results show that the coating thickness increases linearly from 0.031 μm to 7.77 μm with the increase of electroplating time. With the Ni-W coating thickness increasing, the microstructure of fracture changes from cross cracks to straight cracks, the number of cracks per unit area decreases, and the crack spacing increases from 0.79 ± 0.35 μm to 153.56 ± 35.16 μm. The strength and plasticity of samples with Ni-W coating are higher than those of Cu substrate film because of the restriction in dislocation movement and surface work hardening. At the same time, the coating cracks hinder the dislocation movement, absorb energy and restrain the crack growth. When the coating breaks, the dislocation slip behavior will change into plastic deformation, and there is a synergistic mechanism of interface strengthening between the substrate and the coating.

1. Introduction

Ni-W alloy coating has high hardness, high strength, friction and wear resistance, corrosion resistance, thermal stability and other excellent properties [1–5]. It has been widely used in bearing, roller, cylinder, casting mold, special container of petroleum industry and other material surfaces [6–10], and has become the preferred material to replace Cr coating. Ni-W alloy coating can effectively improve the service life of the workpiece in the field of wear resistance and corrosion resistance [11, 12]. The content of W directly affects the microstructure of Ni-W alloy. With the increase of W content, the grain size of the alloy decreases continuously. When the W content is about 19.6 at.%, the Ni-W alloy changes to amorphous state [11]. Both microcrystalline and amorphous Ni-W alloys have the defects of poor plasticity despite their high strength [13].

In recent years, more attention has been paid to the preparation process of Ni-W alloy and its mechanical properties under compressive stress and friction shear stress, and the mechanical behavior of the coated workpiece under uniaxial tensile static load has been ignored. Lv [14] studied the plastic deformation behavior and mechanism of Ni-P amorphous coating on Ni substrate surface. It was found that the Ni-P amorphous coating had good uniform plastic deformation (up to 12%) under the restriction of interface. It can be seen that the interface can effectively improve the plastic deformation ability of brittle coating, but there is less relevant report about the plastic deformation behavior of brittle coating on the plastic substrate. In this study, microcrystalline Ni-W alloy coating was prepared on the surface of cold-rolled Cu sheet by electroplating. The influence of different thickness of Ni-W alloy coating on the plastic deformation...
behavior of Cu substrate was studied, and the synergistic mechanism of mechanical property improvement was analyzed.

2. Experiment

2.1. Materials
Cold rolled Cu sheet is used as plastic substrate. The amount of rolling deformation of the substrate is 97%, and the grain refinement is beneficial to improve the adhesion between the substrate surface and the Ni-W coating [15]. After rolling, a Cu film with a thickness of 300 μm is formed, and then cut into a square with 4 mm × 4 mm as the plastic substrate. The surface of Cu film needs to be polished, degreased and cleaned before electroplating. Then the Ni-W alloy coating is prepared by DC power supply. The electroplating solution formula is shown in Table 1, and the solution is prepared using deionized water. Five kinds of Ni-W alloy coatings with different thickness are prepared by controlling the time. The corresponding deposition time is 0.5 min, 2 min, 5 min, 10 min and 30 min respectively.

| Chemical reagents       | Concentration |
|-------------------------|---------------|
| NiSO₄ · 6H₂O            | 0.06 mol l⁻¹  |
| Na₃C₆H₅O₇ · 2H₂O       | 0.50 mol l⁻¹  |
| Na₂WO₄ · 2H₂O          | 0.14 mol l⁻¹  |
| NH₄Cl                  | 0.50 mol l⁻¹  |
| NaBr                   | 0.15 mol l⁻¹  |
| Temperature            | 65 °C         |
| Current density        | 10 A dm⁻²     |

2.2. Methods
The standard tensile specimen was obtained by wire cutting. The standard distance of the specimen was 4 cm in length and 2 cm in width. The tensile test was carried out by MMT-101NV-10 tensile testing machine with the loading strain rate 1 × 10⁻³ s⁻¹ at room temperature. The stress-strain curves and work hardening curves of different coating thickness were obtained. The microstructure of the coating samples were characterized by S4800 SEM/EDS. The fracture morphology of the samples and the mechanism of coating crack formation were analyzed.

3. Results and analysis

3.1. Relationship between coating thickness and deposition time
Figure 1 shows the curve between Ni-W alloy coating and deposition time. When the deposition time was 0.5 min, 2 min, 5 min, 10 min and 30 min, the coating thickness was 0.031 μm, 0.47 μm, 1.23 μm, 2.67 μm and 7.77 μm respectively. It can be seen that the coating thickness increases linearly with the increase of deposition time. The results are in accordance with Faraday’s law, which shows that the thickness of the coating can be effectively controlled by controlling the deposition time.

3.2. Microstructure analysis of sample interface
It can be seen from figure 2(a) that the interface between Ni-W coating and substrate is clear, the interface is straight and smooth, and no defects such as holes and delamination are found. The microstructure of the coating is compact and the interface is well combined. The grain size of the microcrystalline structure is about 0.3 μm. The EDS spectrum of the sample E with the maximum coating thickness shows that the atomic ratio of W is 15.64% and that of Ni is 84.56% (see figure 2(b)). Figure 2(c) shows the microstructure of Cu substrate after cold rolling. Due to the transverse deformation of the grains under the longitudinal stress during rolling, the grains are refined into long plate shape with a thickness of 0.6–0.8 μm and a overlay lamellar structure.

3.3. Analysis of mechanical properties of samples
Figure 3 shows the stress-strain curves of different samples and Cu substrate. It can be seen from figure 3 that the yield strength and ultimate strength of samples A, B, C, D and E are different with the increase of coating thickness. Although the maximum ultimate strength of E sample is σₘₚₓ = 520 MPa, which is superior to other samples, the yield strength is significantly lower than that of Cu substrate, and the elongation is also lower than...
that of other samples and Cu substrate (table 2), which indicates that large coating thickness restricts its plastic behavior. The curves of A, B, C, D and E in the stress-strain curve in figure 3 also show that the strain of E curve is the smallest, the strain of C and D curve is better than that of E sample and Cu substrate, and the strain buffer curve of A and B curve decreasing is the longest, indicating that the plastic behavior of the sample is excellent.

It can be seen from table 2 that the yield strength $\sigma_{0.2}$, ultimate strength $\sigma_b$, elastic elongation $\varepsilon_e$ and breaking elongation $\varepsilon_f$ are obviously different for samples. The mechanical properties of sample D with the best coating thickness obtained are $\sigma_{0.2} = 423$ MPa, $\sigma_b = 457.59$ MPa, $\varepsilon_e = 1.14\%$, and $\varepsilon_f = 6.72\%$, respectively, which are higher than those of Cu substrate. The results show that the Ni-W alloy coating has a great influence on the plastic deformation of the Cu substrate, and the different thickness of the coating can promote the improvement of the substrate material.

Figure 4 shows the work hardening rate curves of different samples and Cu substrate. It can be found that with the increase of true strain, the value of work hardening rate of the five samples decreased rapidly. The work hardening rate of Cu substrate decreases most obviously. When the true strain is 2.5%, samples A and E have the maximum hardening rate. The hardening rate of the samples in each curve is higher than that of the Cu substrate. The results show that the work hardening ability and uniform deformation ability of the coating samples are improved. When the work hardening rate is zero, necking occurs in different samples and local plastic deformation occurs. The curve in figure 4 shows that the necking of sample E occurs earlier, while the local plastic deformation of sample A lags slightly, which is attributed to the difference of coating thickness.

3.4. Analysis on fracture morphology of samples

As shown in figures 5(a)–(c), the cross-sectional fracture morphology of samples A, C and E are shown respectively. Figure 5(a) shows the fracture morphology of the tensile section of sample A. It can be seen that the Cu substrate has obvious necking, and the Ni-W alloy coating is not evenly distributed on the surface of the substrate. The fracture morphology shows that the Cu substrate has good plastic deformation ability. After necking, the fracture occurs in shear mode, which conforms to the general fracture characteristics of pure metal Cu. In comparison, the coating of sample C in figure 5(b) breaks and separates. In figure 5(c), it is found that the fracture surface of sample E is straight, and there are many steps on the surface, obviously showing brittle fracture characteristics. There are slip bands on the surface of Cu substrate exposed at the fracture of the coating, and the distance between the two sides of the fracture increases with the increase of the deformation. There are continuous slip marks on the surface of Cu substrate, which shows that the coating can effectively limit the plastic deformation of Cu substrate before the coating is broken.

The interaction between Ni-W alloy coating with different thickness and substrate is also different. Figures 5(d)–(f) shows the surface morphology of samples A, C and E after fracture, respectively. As shown in figure 5(d), when the Ni-W alloy coating of sample A is very thin, a large number of intersecting microcracks are generated before the coating breaks, the crack path is relatively zigzag, the distribution is relatively uniform, the crack spacing is very small, about 0.79 $\mu$m, and the angle with the tensile axis is about 60°. The results show that the plastic deformation of Cu substrate affects the formation of initial microcracks in Ni-W alloy coating, and the binding of the coating to the plastic deformation of the substrate is weak. With the increase of the thickness of Ni-W alloy coating, the surface of the coating changes from a curving and variable cross crack to a straight
through crack (perpendicular to the direction of the tensile axis), the number of cracks decreases and the spacing increases. As shown in figures 5(e), (f), samples C and E show that the influence of substrate on the crack growth path of the coating is gradually weakened, and the binding effect of the coating on the plastic deformation of the substrate is enhanced. Transverse cracks (parallel to the stretching axis) were observed in sample E, which may be related to the joint action of stress increase at the coating interface and plastic deformation of the substrate.

3.5. Synergistic mechanism of coating on the plastic deformation of Cu substrate
As shown in figure 6, the relationship curve between coating thickness and crack spacing shows that with the increase of coating thickness, the crack spacing on the fracture surface gradually increases from $0.79 \pm 0.35 \mu m$ to $153.56 \pm 35.16 \mu m$, the number of cracks per unit surface area decreases, and the limiting effect of coating on

![Figure 2. (a) SEM morphology of sample interface; (b) EDS spectrum of coating; (c) SEM morphology of lamellar microstructure.](image_url)
the plastic deformation of substrate increases. This is because the interface binding force between the coating and the substrate will hinder the movement of dislocations and limit the formation of slip lines, resulting in plastic deformation of the bound substrate [16, 17]. In the electrodeposited molten salt system NiSO$_4$·6H$_2$O + Na$_3$WO$_4$·2H$_2$O + NaBr + Na$_3$C$_6$H$_5$O$_7$·2H$_2$O + NH$_4$Cl, a certain amount of Ni and W ions were deposited on Cu sheet. In the electrochemical reaction, W and Cu are immiscible, Ni and Cu are infinitely miscible, and Ni and W are limited to each other. Therefore, Ni can be used to connect Cu and W, and the diffusion reaction can take place between Cu, Ni and W. The precipitated Ni-W microcrystals adhere to the surface of Cu substrate coating. When the grain size is large, the main plastic deformation mode is deformation induced grain coarsening. When the grain size is less than 10 nm, plastic deformation occurs through a grain boundary mediated process similar to mechanically driven grain boundary migration and grain rotation. Figures 7(a) and (b) are the plastic deformation behavior models of composite coating thickness affecting the
Figure 5. Analysis on fracture morphology of sample: (a) fracture morphology of sample A cross section; (b) fracture morphology of sample C cross section; (c) fracture morphology of sample E cross section; (d) surface morphology of sample A after fracture; (e) surface morphology of sample C after fracture; (f) surface morphology of sample E after fracture.
substrate respectively. It can be seen that after the coating fracture, the Cu substrate exposed to the surface, lost the binding of coating interface strength, and there was obvious dislocation slip band along the 45° of the substrate at the fracture. For the sample with thin coating (figure 7(a)), the number of cracks per unit surface area is large and the crack spacing is small, which is conducive to the formation of dense slip lines. However, for the samples with thick coating (figure 7(b)), there are fewer cracks at the fracture site, which limits the plastic deformation of Cu substrate. It can be seen that the crack fracture spacing of the coating plays a major role, and the crack fracture spacing is affected by the thickness of the coating. With the increase of coating thickness, the
crack spacing increases, the number of cracks per unit area decreases, and the channels through which dislocations can escape from the surface decrease. The results show that the increase of dislocation slip resistance is beneficial to the increase of strength, but the plastic deformation ability is decreasing. The analysis shows that the proper thickness of the coating not only has strain hardening ability, but also forms a certain amount of dislocation slip line to promote the plastic deformation. At the same time, strengthening the synergistic mechanism of interface binding force will significantly improve the mechanical properties of the Cu substrate with Ni-W microcrystalline coating.

4. Conclusion

(1) Nanocrystalline Ni-W alloy coating was prepared on the surface of large deformation cold-rolled Cu substrate by electroplating. With the increase of deposition time, the coating thickness increased from 0.031 \( \mu \text{m} \) to 7.77 \( \mu \text{m} \). Compared with Cu substrate the overall strength and plasticity of the composite are improved, showing better work hardening ability. The finite and infinite solid solution and diffusion behavior between Ni, W and Cu atoms are the formation mechanism of strengthening interface.

(2) With the increase of Ni-W alloy coating thickness, the number of cracks per unit area decreased. The crack spacing gradually increased from 0.79 \( \pm \) 0.35 \( \mu \text{m} \) to 153.56 \( \pm \) 35.16 \( \mu \text{m} \), which resulted in the change of the coating from a variable cross crack to a straight through crack. This is due to the joint action of the increase of the internal stress in the interface and the plastic deformation of the basement.

(3) The interface bonding force of Ni-W alloy coating hinders the dislocation slip movement of Cu substrate, increases the strain hardening ability and improves the tensile strength. The fracture spacing and number of cracks are determined by different coating thickness. The appropriate thickness of the coating can facilitate the formation of dislocation slip and improve the plastic behavior of the samples.

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