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# Fabrication of Nanostructured Electroforming Copper Layer by Means of an Ultrasonic-assisted Mechanical Treatment

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**Abstract**

Electroformed copper layer with nanostructure is obtained using a subsequent mechanical treatment under the conditions of ultrasonic vibration according to the demand of high performance material in aeronautics. The microstructure of the electroformed copper layer is observed by optical microscope (OM), scanning electron microscope (SEM) and transmission electron microscope (TEM). The tensile strength is evaluated with a tensile tester. It is found that bulk crystal of electroformed copper's surface layer is changed to nanocrystals (about 10 nm in size) after the ultrasonic-assisted mechanical treatment (UMT) but the whole monocrystalline structure still remains. The tensile strength exhibited by the new copper layer is two times better than the regular electroformed copper layer, while the fracture strain remains constant. In addition, the strengthening mechanism of UMT process is proved to be dislocation strengthening mechanism.

*Keywords:* electroformed copper layer; nanostructure; ultrasonic-assisted mechanical treatment; tensile strength

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## 1. Introduction

Electroforming as a special process technique has been used for the preparation of metal components due to its low cost and high copying accuracy. Moreover, final product can be attained directly by electroforming without further processing. Electroforming, as a precise technology, can satisfy industry demands of precision, complex and superfine metal parts. So it is widely used in many industries such as auto, electron, material, aviation and aerospace. In recent years, the preparation of high performance materials by electroforming has gradually become a hot topic[1-3].

Traditional ways to prepare nanostructured layers, such as pulse electrodeposition[4], laser plating[5] and jet plating[6] are usually limited to the operation condition, the high temperature and vacuum condition. Ultrasonic wave assisted electroplating is another way to obtain nanostructured electrodeposites. A great number of studies have shown that the ultrasonic vibration effects can accelerate mass transport, increase the number of nucleation, inhibit excessive growth of grain, decrease the overpotential of polarization and enhance the preferred orientation, etc[7-11]. However, many researchers pay full attention to the conditions or parameters of the plating process and few reports about nanostructured depositions obtained by subsequent ultrasonic-assisted technique are found.

It was found that the formation of the nanostructure is mainly caused by plastic deformation-induced grain refinement, which has been extensively investigated in various metals and alloys over the past decades. Accordingly, several relevant techniques have been developed rapidly such as friction sliding[12], surface mechanical attrition treatment (SMAT)[13], surface mechanical grinding treatment (SMGT)[14] and wire-brushing[15]. These subsequent treatments can effectively avoid the influences of the plating parameters. But some of these methods suffer from limited nanostructured layer thickness or structural inhomogeneity of the surface layer[14]. In tiny metal part electroforming field, the required components are micro-sized, precise, complex and superfine. For example, waveguide tube, which is micro-sized in shape, needs to have a high performance to meet the requirements in aeronautics. These processes such as SMAT or SMGT obviously cannot satisfy the demand of the electroforming tiny components because of the high attrition force.

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Herein, a novel technique named ultrasonic-assisted mechanical treatment (UMT) is developed in our work to synthesize a nano-structured electroforming copper layer. UMT is a mechanical treatment process, i.e., vibrating glass balls act on the surface of electrodeposite under the conditions of ultrasonic irradiation. The merits of this method include no complicated condition requirement, easy operation and little physical damage to micro metal parts. Therefore, it is a new attempt to study the ultrasonic effects and its application in microparts electroforming.

## 2. Experimental

Copper layers were electroformed from an acid sulfate bath consisting of copper sulfate (200 g/L), sulfuric acid (60 g/L) and hydrochloric acid (30-100 mg/L). The chemicals of analytical grade and distilled water were used to prepare the solution. The temperature of solution was kept at (25±1)°C and the current density was maintained at 5 $A\cdot dm^{-2}$. And the average thickness of electroformed copper was about 200 μm. An electrolytic copper (99.99% Cu and 0.01% P) served as anode while a aluminum foil plate (with dimensions of 50 mm × 20 mm × 50 μm) served as cathode. After electrodeposition, the cathode was immersed in a sodium hydroxide bath (about 80 °C) for several minutes to dissolve the aluminum foil and then electroformed copper layer was obtained.

After electroforming, the copper layer was put into the UMT device. The schematic illustration of UMT setup is shown in Fig.1. The electroformed copper layer was put on the bottom of a 250 mL Bunsen beaker which was placed in the middle of a SCQ-2201A ultrasonic vibrator (the wave frequency is 48 kHz, the power is 180 W and the volume of the ultrasonic vibrator is 3 L). Both the ultrasonic vibrator and the Bunsen beaker were filled with water. Glass balls with density of 2.5 $g/cm^3$ and diameters (∅) of 1 mm and 2 mm (balls of ∅ 1 mm with weight percentage of about 70% and the total weight was 10 g) were dispersed evenly on the copper surface and completely covered the sample. Under the conditions of ultrasonic the glass balls jumped and rolled incessantly and provided mechanical impinging to the surface of copper layer. Although the ultrasonic vibration lasted 2 h, the copper specimen had not been oxidized in water because the speed of the balls polishing was faster than that of oxidization.

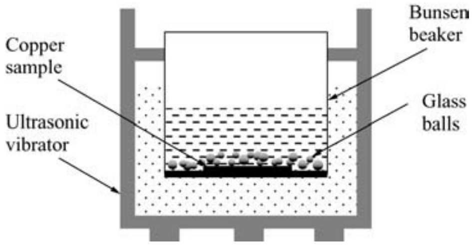
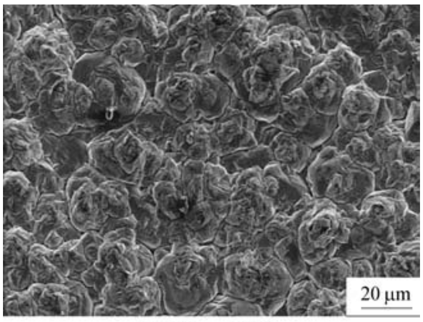


Fig.1 Schematic illustration of UMT setup.

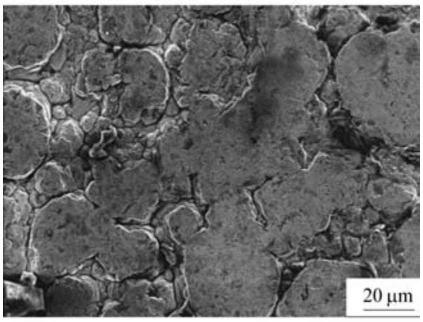
The surface morphologies were analyzed by scanning electron microscope (SEM, JSM-5800, 10 kV). The cross-section micrographs were investigated by optical microscope (OM, OLYMPUS-BX51N). The cross-section micrographs of the electroformed copper's surface layer were observed by transmission electron microscope (TEM, JEM-2100F, 200 kV). The tensile strength tests were carried out on a MTS-880 tester with the crosshead speed of 2 mm/min and tensile direction was parallel to the long edge of the sample.

## 3. Results and Discussion

Fig.2 shows the SEM surface images of electroformed copper layers with and without UMT. The surface of the copper layer without UMT takes on a cauliflower structure[16] as shown in Fig.2(a). After UMT, the cauliflower-like grains are crushed to flat shape by the jumping balls and the percussion marks can be found in Fig.2(b). The protruding summits are worn out and the surface is polished.



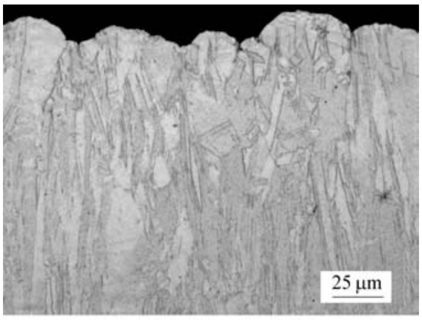
(a) Without UMT



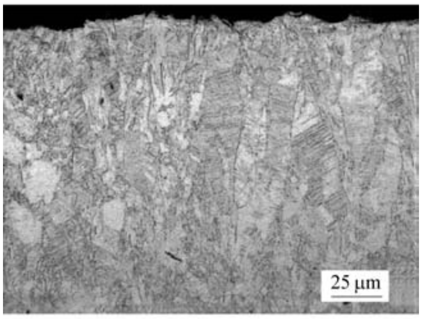
(b) With UMT

Fig.2 SEM surface images of electroformed copper layers.

Fig.3 shows the cross-section pictures of electroformed copper layers with and without UMT. Meanwhile, contrasting the section morphologies of the copper layer with and without UMT, it is found that bulk and columnar crystals (see Fig.3(a)) are crushed into small and unevenly distributed pieces (see Fig.3(b)) after UMT. And the surface of the copper layer became smooth, but the columnar shape remains. The cavitation effects and micro-streaming caused by ultrasound are thought to be two main mechanisms in chemical process. The cavitation bubbles implode and produce the local high temperature and pressure, which can affect the degree of mixing, the mass transfer coefficient values, the residual deformation and so on[7-11]. After the glass balls are added to the system, the power of cavitation effects is transformed to mechanical energy of the vibrating glass balls, which collide with the surface of electroformed copper layer, change its morphology, and refine the grains.



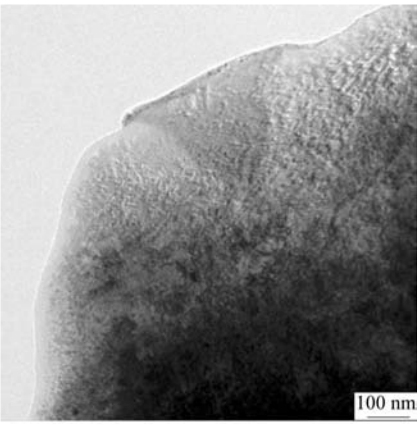
(a) Without UMT



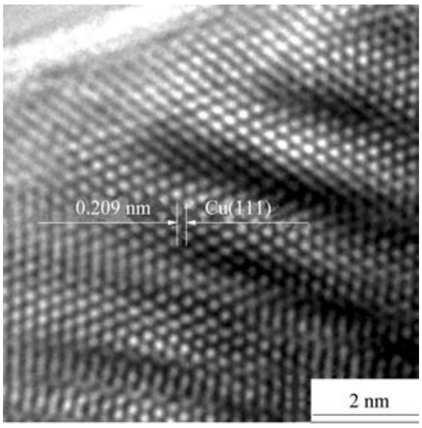
(b) With UMT

Fig.3 OM cross-section micrographs of electroformed copper layers.

To further investigate the structural differences, TEM and high-resolution TEM (HRTEM) cross-section images of the copper layer with and without UMT are tested. The results are shown in Figs.4-5.

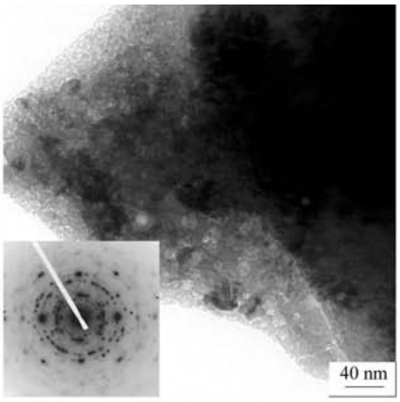


(a) TEM crosss-section micrograph

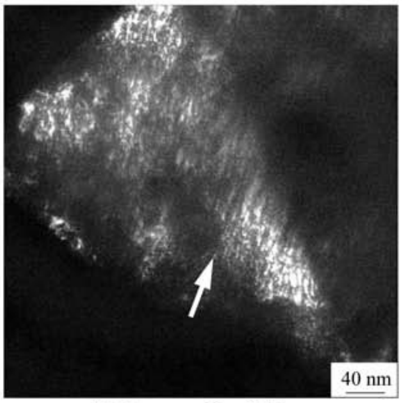


(b) HRTEM image

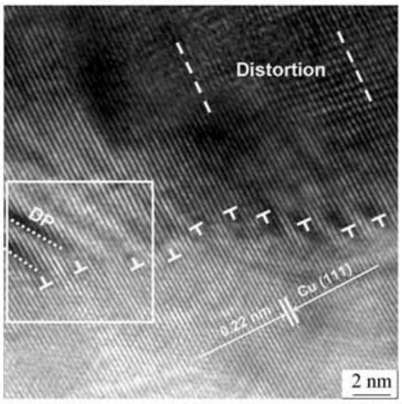
Fig.4 TEM crosss-section micrograph and HRTEM image of electroformed copper layer without UMT.



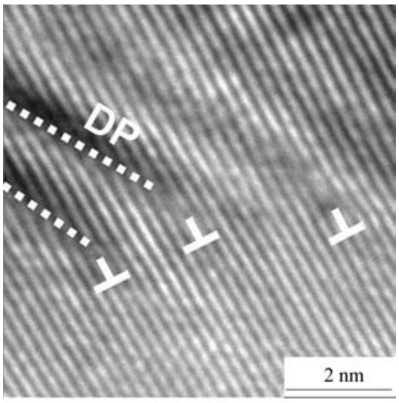
(a) BF micrograph (inset shows the SAED pattern)



(b) Corresponding DF image



(c) HRTEM image (symbol “⊥” represents dislocation)



(d) Enlarged view of white plane of Fig.5(c)

Fig.5 TEM crosss-section micrographs and HRTEM image of electroformed copper layer with UMT.

Bulk crystal of the copper layer without UMT can be found in Fig.4(a). The interplanar spacing is calculated to be about 0.209 nm, which matches well with the standard d-spacing of Cu (111) as illustrated in Fig.4(b).

Plan view of TEM bright-field (BF) and dark-field (DF) images in Fig.5 shows the equiaxed nano-grains (about 10 nm in size) of electroformed copper's surface layer after UMT. Nano-grains obtained by UMT have obviously preferred orientation and the orientation is the arrow pointing direction as shown in Fig.5(b). The corresponding selected-area electron diffraction (SAED) pattern (inset of Fig.5(a)) with concentric rings inside and diffraction spots outside indicate the polycrystalline nature of nanocrystals and monocrystalline of bulk crystal, respectively. Hence, it can be concluded that the bulk crystal of the copper's surface layer is crushed into nanocrystals but the monocrystalline feature of electroformed copper still remains.

Fig.5(c) and Fig.5(d) show HRTEM images of copper layer with UMT, and Fig.5(d) is the enlarged view of Fig.5(c). Linear arranged edge dislocations and dislocation pile-up (DP) can be clearly identified in these images. And the lattice distortion caused by collision of the glass balls can also be observed. Strengthening mechanisms in electrodeposits generally include fine grain strengthening, the second phase strengthening, work hardening, DP strain hardening and strengthening by coherent internal boundaries at the nanoscale[17-20]. Based on the experimental results obtained, it can be concluded that the main reasons for copper layer being strengthened are proliferation and movement of dislocations.

The movement process of dislocation can be described as follows. Firstly, stress concentrates on the surface of copper specimen due to the jumping glass balls during the UMT process and linear arranged dislocations form at the stress concentration area as shown in Fig.5(c). Secondly, dislocation glide leads to short-range dislocation interactions and long-range interactions, simultaneously involving the formation and removal of deformation-induced boundaries as the strain is increased[21]. Finally, multiple DP forms when the dislocations are blocked. The slippage of the dislocations is hindered and the resolved shear stress along the slipping direction is increased. According to the Schmid law[22], the tensile strength ($\sigma$) is proportional to the resolved shear stress ($\tau$) by the relation $\sigma=m\tau$, where $m$ denotes Schmid factor. As learned from the equation, increasing $\tau$ caused by dislocations leads to enhancing $\sigma$.

Consequently, the nano size grains and a large number of dislocations piled up within the copper specimen are obtained. The increase of intragranular dislocation density and lattice distortion results in the increase of the number of new grain nucleation and formation of small grains. The strengthening mechanism of UMT process is thought to be dislocation strengthening mechanism.

To confirm the strengthening mechanism, tensile strength of the copper specimen with and without UMT is tested as observed in Fig.6. The electroformed copper with nanocrystal structure exhibits a double higher tensile strength than that of the electroformed copper layer without UMT. However, their fracture strains are both about 15%, which shows that the plasticity of the copper layer remains constant after UMT. Thus, the tensile test results conform to the above morphological analysis.

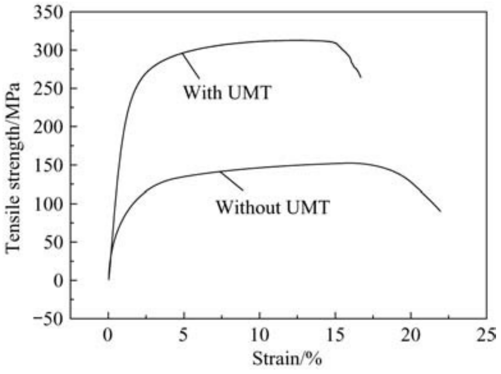


Fig.6 Tensile curves of electroformed copper layers with and without UMT.

## 4. Conclusions

In conclusion, a novel technique UMT, as the subsequent treatment after electroforming, is developed to obtain nanostructured copper layers.

(1) Bulk crystal of electroformed copper's surface layer is crushed to nanocrystals (about 10 nm in size) via the glass balls driven by ultrasonic vibration but the whole monocrystalline structure still remains.

(2) The electroformed copper strengthened by the UMT process with the dislocation strengthening mechanism exhibits a double higher tensile strength compared with the copper layer without UMT, while the fracture strain remains constant.

(3) The reported UMT approach has paved a new

way towards high performance nanostructure electroforming.

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