Effect of Thiourea on the Nanocrystalline-Copper Coating Prepared by Jet Electrodeposition

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Jet electrodeposition with the aid of thiourea was proposed in this paper to improve the deposition quality of copper coatings. The effects of the content in the electrolyte on the coating microstructures, morphologies and mechanical performances were examined. The results show that a dense nanocrystalline copper coating is fabricated with 10 mg/L thiourea addition. The average crystal size attains 29 nm. The preferred crystal orientation varies from (111) to (220) as the thiourea content in the electrolyte rises to 10 mg/L from 5 mg/L. The microhardness increases by 81%, and the tensile strength increases by 51%, using current density 400 A/dm^2 and at the thiourea concentration 10 mg/L.

1. INTRODUCTION

Nanocrystalline copper has received much attention due to the high electrical conductivity and good mechanical properties [1-3]. Nanocrystalline copper is widely applied in electrical switch contacts, tool electrodes and interconnect materials for printed circuit boards [4-6]. Currently, there are a number of methods for nanocrystalline copper preparation [7-10], among which the electrodeposition method brings special benefits, such as simplicity, economy and wide application range of materials. However, the low production rate restricts the further application of electrodeposition, since the deposition rate of the conventional electrochemical deposition is generally only approximately 1.5-2 μm/min [11,12].

Jet electrodeposition (JE) is a recently emerging coating method [12-18] and is expected to solve the above challenge. As shown in Fig. 1a regarding the fundamental principal of JE, the electrolytic jet

sprays from a nozzle to the cathode and continues providing fresh electrolytes to the deposition area, which results in deposition at a substantially higher rate than the conventional electrodeposition (the rate is approximately up to 40 µm/min) [11,12]. Therefore, a much higher current density can be applied in JE, which results in the high increase in nucleation and the refining of the grain size. However, since the deposition rate and coating quality are often known contradictory in the electrodeposition application [13], at high current density, the deposit coating tends to grow in porous cells and eventually forms a serious dendritic growth after it exceeds a number of scanning depositions (see Fig.1b). It can be difficult to obtain a thick bulk material and deteriorate the mechanical properties of the coating. Currently, the methods to improve the electrodeposited surface include air agitation, supersonic vibration, use of a pulsed current (PC) and the addition of surfactants [14-21]. Thiourea (TU) has the function of levelling and refining grains and is widely used in the electrolytic refining of copper [21-25]. Fan examined the effect of thiourea on the Cu-Al_2O_3 composite coating preparation and found thiourea has the function to attract Al_2O_3 NPs to the electrolyte and generate the synergistic effect to enhance Al_2O_3 content in the composite coating [26]. However, there are rarely applications of thiourea in the preparation of pure nanocrystalline copper by jet electrodeposition, and its effect to improve the deposition quality and restrain the nodules, dendritic or other defects, generated at high current density in jet electrodeposition, has not been studied.
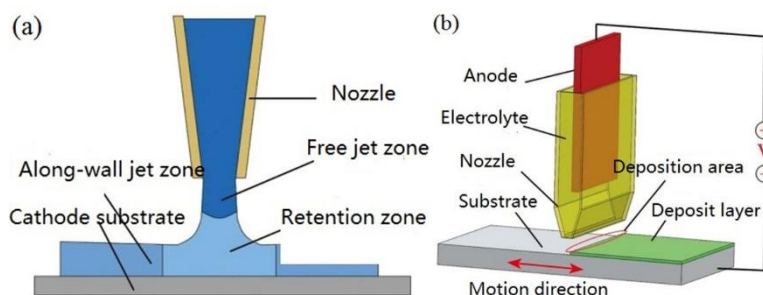

Figure 1. Schematic diagram for typical jet electrodeposition process

The present study examines the influence of the thiourea addition during the jet electrodeposition process. The microstructure, morphology, and crystalline orientation of the nanocrystalline coatings for different thiourea content in the electrolyte were analysed. It also discussed how the thiourea concentration and other experimental parameters affect the coatings properties, in order to obtain the optimized technical configuration.

2. EXPERIMENTAL

2.1 Experimental configuration and conditions

A JE experimental facility (see Fig. 2) was used to prepare the nanocrystalline copper coatings. A copper bar was fixed inside the nozzle to act as the anode material. The 304 stainless steel with size

70 mm×15 mm×1.5 mm was used as the cathode material. Table1 describes the electrolyte composition and experimental conditions.
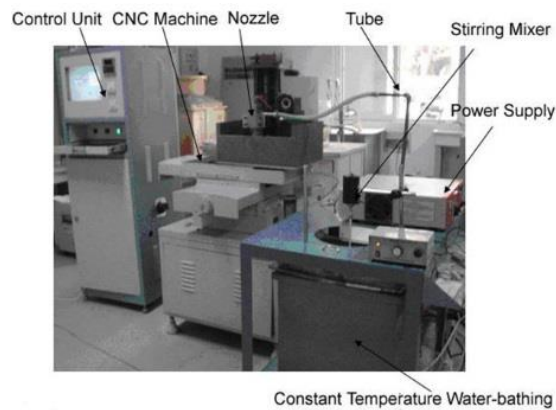

Figure 2. On-site photo of the experimental machine for jet electrodeposition

2.2 Examination of nanocrystalline coatings

An LEO-1530 scanning electron microscope, manufactured in Japan, was used to observe the coating morphology and microstructure. An X-ray diffraction spectrometer was used to examine the coating material microstructure. An HVS-1000A microhardness meter was applied to measure the coating hardness with 100 g load. A universal testing machine (manufactured in China) was used to test the tensile properties.

Table 1. Electrolyte composition and experimental conditions

Electrodeposition bath and process	Composition and condition
$CuSO_4 \cdot 5H_2O$	250 (g/L)
H_2SO_4	50 (g/L)
Thiourea	0-20 (mg/L)
Temperature	40 ±2°C
Nozzle size	rectangular (20 mm×1 mm)
Spray distance	5 mm
Electrolyte flow velocity	10 m/s
scanning rate	1000 mm/min
Current density	200-500 (A/dm^2)
Deposition time	30-120 min
Deposition layer	400-3000 layers

3. RESULTS AND DISCUSSION

3.1 Effect of thiourea and deposition layers on the coating surface morphology

Fig.3 shows at current density 200 A/dm^2, how the surface morphology changes with the thiourea concentration variation. At first, without thiourea added, the deposit surface experiences obvious nodules

growth sized 20-30 μm (in Fig.3a). However, when the thiourea concentration rises, the size of nodules decreases with surface gradually flattening. Once the thiourea addition rises to 5 mg/L, only a few slight bumps can be observed (Fig.3b). As 10 mg/L amount of thiourea was used, the coating surface reaches the flattest and smoothest (Fig.3c). However, as more than 10 mg/L thiourea applied, the coating surface quality adversely decreases, and micro-pores appear on the deposited surface (Fig.3d). Therefore, increasing the thiourea concentration does not always have the function to improve the surface morphology. In addition, 10 mg/L thiourea concentration may have the optimal effect of morphological improvement.
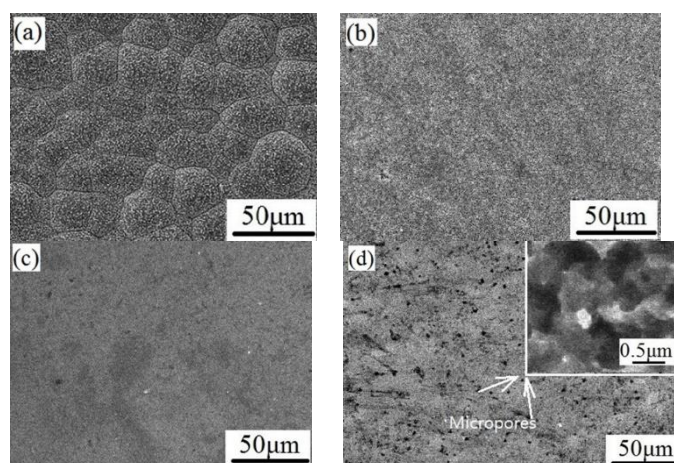

Figure 3. Surface morphology of the copper coating at different thiourea addition including (a) 0 mg/L, (b) 5 mg/L, (c) 10 mg/L, and (d) 15 mg/L

The surface morphology after a number of deposited layers using the electrolytes with and without the addition of thiourea, is shown in Fig.4. In the absence of thiourea, when 400 layers are deposited, the surface of the deposited surface is flat and acceptable. After 1000 layers are deposited, the cell-like protuberant nodules become thick and increasingly grown. After 1600 layers, at approximately 920 μm thick, the cell-like nodules expand to a size of 50-60 μm. From these layers (1600), the deposition quality begins to rapidly deteriorate, so the deposit process cannot be continued, which implies that the deposit coating with a certain thickness cannot be achieved at this circumstance. The deposited surface becomes gradually composed of cellular particles when the number of deposition layers increases because of the particular growth pattern of the grains that deposit on the cathode. Under the electrical field generated by jet electrolyte, the copper grains grow at different rates, and their individual size differs accordingly. With the increase in number of layers, the growth rate of large grains is much faster than that of small grains. Finally, many small grains tend to stop growing as the big grains shielding the electric field from the exposure. Hence, the number of big grains increases, and voids are formed among the large grains, which leads to a significant decrease in compactness of the deposition layer. The formation and rapid growth of large grains also greatly increase the surface roughness and worsen the deposition quality.
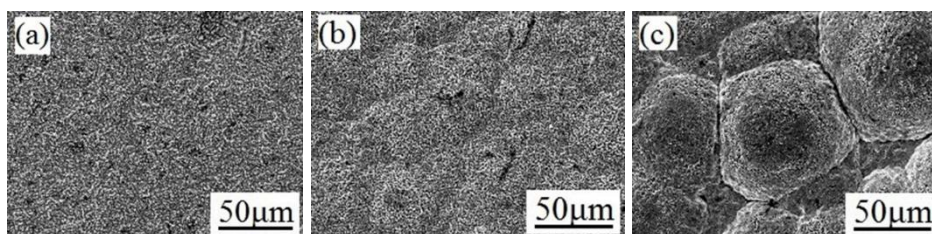
Figure 4. Surface morphology of the nanocrystal copper coatings with 10 mg/L thiourea concentrations of (a) 400 layers, (b) 1000 layers and (c) 1600 layers

In comparison, adding 10 mg/L thiourea in Fig. 5, when the deposition layers increase from 400 to 1000 and even 2800, the deposit surface morphology continually remains unchanged and flat without cell-like particles being observed. This improvement allows the scanning deposition to continue layer by layer. With the current density 200 A/dm^2 and the thiourea concentration 10 mg/L, a thick bulk copper with a nanocrystalline structure and good surface quality is prepared at deposition layer 3000, which is approximately 2.0 mm thick, and at layer 2500, which is approximately 1.5 mm thick.
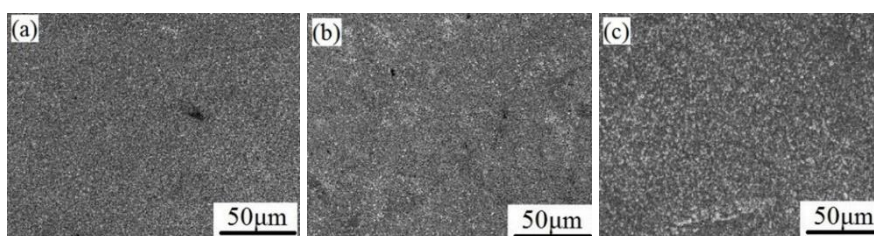

Figure 5. Surface morphology of the copper coatings without the addition of thiourea of (a) 400 layers, (b) 1000 layers, and (c) 2800 layers

The effect of the thiourea additive on the surface morphology of the deposit layer is mainly due to the grain refinement effect of the thiourea addition. First, the active site of the crystal can be covered by the thiourea, which insulates the nearby atoms to adsorb to the crystal growth point to restrain the crystal from grown-up. Additionally, the cathode overpotential is increased by the added thiourea, which generates more nucleation so as to reduce the grain size. These results support the generation of flat and smooth copper deposit surface. Whereas, a too high thiourea concentration cannot induce the crystal refining. On the contrary, the element of sulfur from the thiourea can generate stress inside the coating, and cracks and pores can be formed, which makes the coating brittle and inhibits the nucleation [25-28]. This phenomenon may explain the reason why too high thiourea content increases the crystal size and weakens the coating properties. This phenomenon will be proven by the following presented microstructures and mechanical properties in comparison with various concentrations of thiourea added in the electrolyte.

3.2 The effect of thiourea addition on the copper coating microstructure

The thiourea addition also has some effect on the microstructure, with the given current density of 200 A/dm^2. As shown in Fig. 6 about the cross section of the samples, as the thiourea added changing within the range of 0-15 mg/L, the coating material experiences the variation from the porous microstructure to a compact, uniform and refined microstructure. Once the added thiourea rises to 10 mg/L, the deposits exhibit the most compact status and form a typical microstructure that contains nanocrystals (Fig.6c). Afterwards, the microstructure begins to deteriorate with the appearance of small holes, cracks and defects, and the deposition layer deteriorates (Fig.6d), if the thiourea concentration increases.
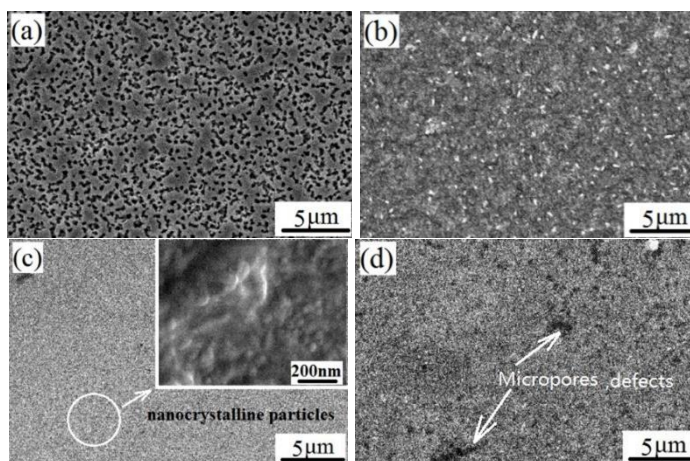

Figure 6. Microstructure variation of the coatings with thiourea concentrations of (a) 0 mg/L, (b) 5 mg/L, (c) 10 mg/L, and (d) 15 mg/L
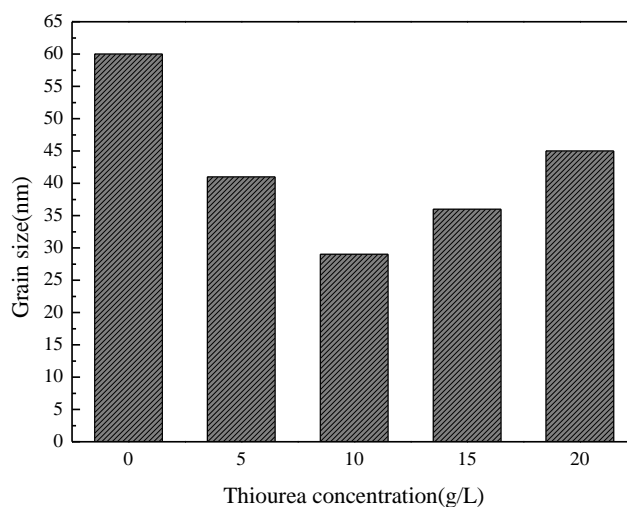

Figure 7. The relation between the coating crystal size and the thiourea concentration

Fig. 7 indicates that thiourea also affects the coating's crystal size. When thiourea is not added, the average crystal size is approximately 60 nm. The results show that the crystal size reduces with the

increase of thiourea. With 10 mg/L thiourea used, the crystal decreases to the size of 29 nm. But, if the thiourea rises to 15 mg/L, the grains size begins to grow and reach the maximum 45 nm.

Meanwhile, from Fig.8, it can be observed that the thiourea concentration also significantly affect the crystal preferred orientation of the coating material. It can be observed within 0-10 mg/L thiourea addition, the strongest intensity can be found for the (111) plane which belongs to the preferred orientation. However, as the thiourea addition rises to the scope of 10-15 mg/L, the (220) plane gradually replaces the (111) plane as the new preferred orientation, with the strongest intensity. Interestingly, during the change of thiourea addition, there are rarely preferred orientation because the intensities of crystal planes are almost close, which only occurs at the time of 10 mg/L thiourea added.
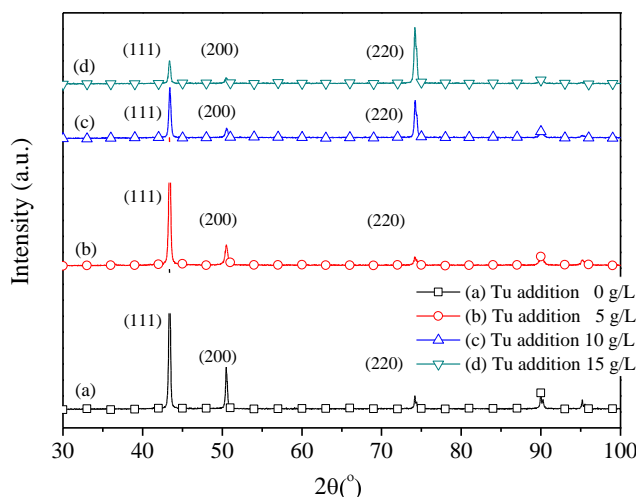

Figure 8. Coatings crystal preferred orientation with different thiourea concentrations

The effect of thiourea additive on the microstructure of the deposit layer also mainly lies in the grain refinement. As mentioned above, thiourea molecule can effectively adsorb on the active point of the deposited layer and prevent the diffusion of the adsorbed atom to the active point. The concentration of the adsorbed atom on the crystal plane increases sharply, resulting in the increase of the crystal overpotential, which favours the formation of new crystal nuclei and decrease the grains size.

*3.3 Effect of thiourea addition on the coatings mechanical property*

Fig.9a shows the relations among the microhardness and the current density and thiourea addition. At first, within the range of 200-400 A/dm², as the current density rising, the microhardness continues to rise. Afterwards, as the current density increasing, the microhardness decrease correspondingly. Additionally, with a same current density, the value of microhardness is observed to rise with the increasing thiourea addition in the range of 0-10 mg/L. When the current density set 400 A/dm² with the thiourea addition 10 mg/L, the maximum microhardness 2.65 GPa is derived, which is 81% higher than the minimum microhardness 1.46 GPa, produced at current density 500 A/dm² and

without thiourea added. After the thiourea addition exceeds 10 mg/L, the microhardness of the corresponding copper coating gradually decrease, which indicates that a higher thiourea content have a curing effect. These results show that the addition of thiourea and appropriate technical conditions are helpful to improve the mechanical properties of the copper coating.

From the above analysis, two reasons favour the increase of hardness: the first one is amount of thiourea, which significantly refines the copper-plated coating grains, as proven by grains size comparison in Fig.7, and strengthens the microstructure of the coating, as shown in Fig.3 and Fig.6. Second, the application of a high current density can promote the nucleation and grain refinement of the copper coating, so the microhardness of the copper coating can be significantly improved, Simultaneously, the enhancement effect of the high current density is guaranteed under the action of thiourea because it inhibits the excessive growth of grains and weakens the negative effect of the high current. However, the improvement effect of thiourea is limited. Once the current density is over-high, numerous large nodules will form on the deposited surface, and cracks will occur among the grains. When the current density exceeds 400 A/dm^2, the microhardness will be seriously reduced. The experimental phenomena are also proven in reference [27-29].

As shown in Fig.9b, the way that thiourea addition and current density affects the copper coating tensile strength in an alike tendency with that in Fig.9a about the microhardness variation. Specifically, the maximum value 602 MPa of tensile strength occurs at 400 A/dm^2 current density, 10 mg/L thiourea concentration. Compared with the minimum value 431 MPa gained at 500 A/dm^2, the maximum value increases by 41%. Fig.9c displays how the thiourea addition affect the elongation of the coating. Within the current density range of 200-500 A/dm^2, the elongation decreases with the increasing current density.

Meanwhile, for a given current density, as increasing thiourea concentration, the elongation continuously decreases within the range of 0-15 mg/L thiourea concentration. The maximum elongation is 8% when the current density is 200 A/dm^2 and no thiourea added while the minimum value 1.7% is obtained at the current density 500 A/dm^2 and 15 mg/L thiourea added. The experimental results show that the increase of both the thiourea content and the current density has a general negative influence on the coating's plasticity. According to the literature [30,31], if an over-high current density applied, the precipitation of hydrogen will become serious and result in internal stress. Moreover, with the increase in thiourea concentration, the sulfur content in the deposit also increases, which gradually makes the deposit brittle and reduces the plasticity.
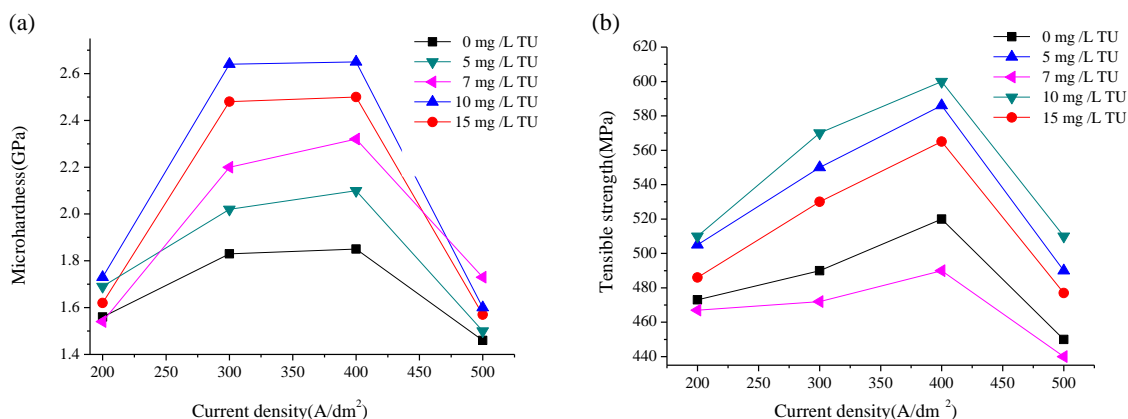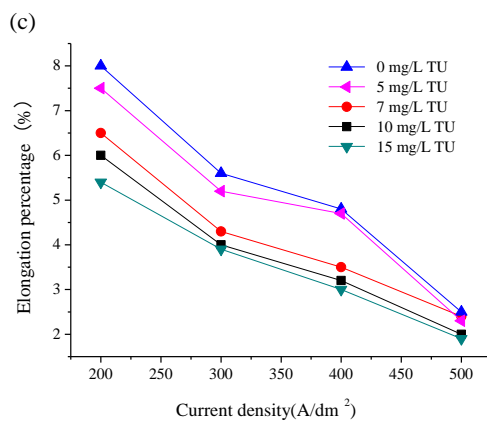
Figure 9. The relationships between the thiourea concentrations and the mechanical properties including the (a) microhardness, (b) tensile strength and (c) elongation percentage

The tensile fracture morphology of the coatings also varies with different thiourea concentrations. Fig.10a shows that there are many deep pits on the fracture section, i.e., dimples, which indicate that the deposits are plastic. However, at a given current density, with the increase in thiourea content, the pits become shallow and scale-like that occurs with 10 mg/L thiourea addition. It indicates the plasticity of the deposited coating decreases to a relatively low level. With the addition of thiourea, the copper coating material becomes more brittle, and the plasticity decreases, which is also consistent with the properties in the tensile curve of Fig.9c, as proved in literature [32].
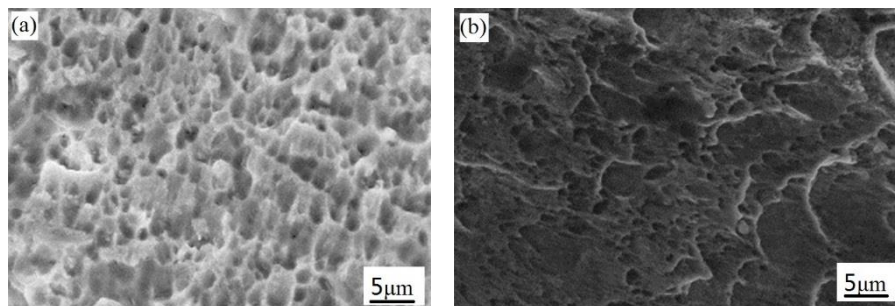

Figure 10. Copper coating fracture morphology at thiourea concentrations: (a) 0 mg/L and (b) 10 mg/L

4. CONCLUSIONS

Nanocrystalline copper was prepared using jet electrodeposition with the addition of thiourea concentration. It has been proved the addition of thiourea has function to improve the coating surface morphology and its microstructure.

By using 10 mg/L thiourea, a smooth and flattened coating surface morphology was derived with compact microstructure and the crystal size below 30 nm. The bulk material and smooth surface were fabricated using a current density of 200 A/dm^2 and 2500 and 3000 deposition layers at the thickness of 1.5 and 2 mm.

The maximum hardness of 2.65 GPa was obtained at 400 A/dm^2 current density as well as 10 mg/L thiourea addition. With the same optimized parameters combination, the tensile strength had a maximum value of 602 MPa.

CONFLICT OF INTEREST

The authors declare that there is no conflict of interest regarding the publication of this paper

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