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Short Communication

Effects of Laser Irradiation on a Copper Electrodeposition Process and Coating Quality

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In this study, a hybrid pulsed laser and electrochemical processing technique was used to deposit a copper coating on a stainless steel substrate. The laser irradiation mechanism in the electrodeposition process was studied by detecting the mechanical and thermal effects. The electrodeposition samples were irradiated by lasers with varying single-pulsed energies and compared. The grains of the coating were observed with a scanning electron microscope (SEM), and the tensile strength and ductility were measured using a UTM4000 series electronic universal testing machine. The results showed that the deposition rate may be increased, and the coating quality may be improved by laser irradiation with the proper single-pulsed energy. This is due to an increase in the conductivity and diffusion coefficient of the solution, arising from an increase in the solution temperature and the local stirring induced by plasma bubbles. The grain size and growth direction of the dendrite are also affected by laser irradiation.

Keywords: Pulsed laser; Electrodeposition; Deposition rate; Coating quality; Plasma shockwave

1. INTRODUCTION

Electrochemical machining has become an attractive area of research due to its unique advantages [1,2]. Composite processing by electrodeposition coupled with other techniques, such as using magnetic fields or ultrasonic energy, can reduce the defects from traditional electrodeposition processes to acquire deposits of better quality [3,4,5]. Characterized by its high energy, good directionality and other advantages, laser irradiation has become widely used in electrodeposition processes.

V.I. Grishko studied the effect of laser irradiation on the electroplating of gold, copper and nickel. The results suggested that laser irradiation can improve the electroplating efficiency due to a thermal gradient in the electrolyte generated in the vicinity of the laser focal point [6]. A high-aspect-ratio 3-D electroplating technology assisted by laser irradiation was studied by Jungwoo Park, in which tall, narrow, three-dimensional microstructures were electrodeposited [7]. Yan Tao used laser irradiation to brush plate nickel on a stainless steel substrate and found that the hardness of the coating was 56 percent higher than that of coatings generated from normal brush plating. This is due to refinement of the grains caused by laser irradiation [8]. Qiong Nian studied a laser assisted electrodeposition technique to deposit Cu_2ZnSnS_4 (CZTS) on a photovoltaic thin film at room temperature and standard atmospheric pressure. It was found that the deposition rate may increase and the quality of the CZTS thin film may improve by laser assisted electrodeposition [9].

In this work, a processing system, including the detection equipment, was developed from the combination of laser irradiation and electrodeposition. The mechanical and thermal effects induced by the laser in the electrodeposition process were investigated, as well as the mechanism. Furthermore, the surface morphology of the coating was observed, and the tensile strength was measured. The effects of laser irradiation on the rate of electrodeposition and the quality of the coating were analyzed. The results showed that laser irradiation drastically decreased the grain size, improved the tensile strength and significantly increased the deposition rate.

2. MATERIALS AND METHOD

2.1 Materials

In this work, the cathode substrate material was a 30 mm×12 mm×2 mm piece of stainless steel. Prior to the experiment, the cathode substrate was ground, acid pickled and washed, and the oil was removed. The anode was a 50 mm×60 mm×5 mm piece of pure copper. The concentration of each component of the electrolyte solution is shown in Table 1.

Table 1. Concentration of each component

Component	$CuSO_4{\cdot}5H_2O$	H_2SO_4	NaCl
Concentration	0.88 mol/L	0.6 mol/L	2.73×10^{-3} mol/L

To reduce the internal stress and improve the brightness of the coating, sodium chloride (NaCl) was added to the solution. NaCl can also improve the conductivity of the solution.

2.2 Method

2.2.1 Laser and electrodeposition composite processing

The cathode was fixed on the bottom center of a deposit tank with a special fixture, as shown in fig. 1. The size of the deposit tank was 120 mm×100 mm×80 mm. The concentration of an electric field on the cathode edge can lead to the overgrowth of deposited material. [10] The deposit area was confined to a size of 3 mm×4 mm, and the remaining area was insulated to avoid edge overgrowth. In the laser and electrodeposition composite processing, a pulsed fiber laser was used, which had a frequency of 20 kHz, a wavelength of 1064 ns and a spot diameter of 50 μm. The laser was focused 1 mm above the cathode to avoid the ablation of the cathode substrate and the coating.

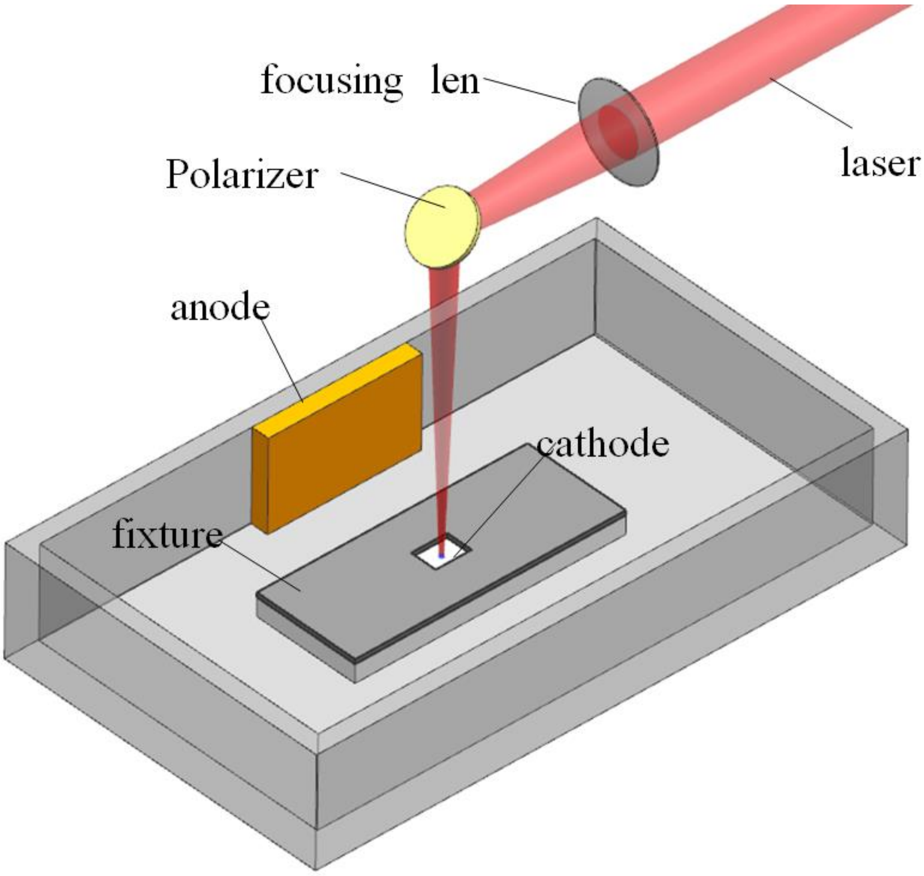

Figure 1. Schematic of laser and electrodeposition composite processing

The laser was scanned at a speed of 200 mm/s by changing the angle of the polarizer, and the single-pulsed energies were 0 mJ, 0.2 mJ, 0.4 mJ, 0.6 mJ and 0.8 mJ. The anode was placed perpendicular to the cathode and attached to the inner wall of the deposit tank. The cathode and anode were dipped in the electrolyte solution. The liquid level was higher than the cathode substrate by approximately 4 mm. The experimental system is shown in fig. 2. The parameters for the pulsed power supply used in this experiment are shown in table 2. The experiments were carried out at room temperature.

Table 2. Power supply parameters used in the experiment

Parameter	Frequency	Duty cycle	Average current	Pulse width
Value	2 MHz	40%	10 mA	200 ns

The laser and pulsed power supply were controlled by a computer. The deposition time for each experiment was three hours.

2.2.2 Process detection

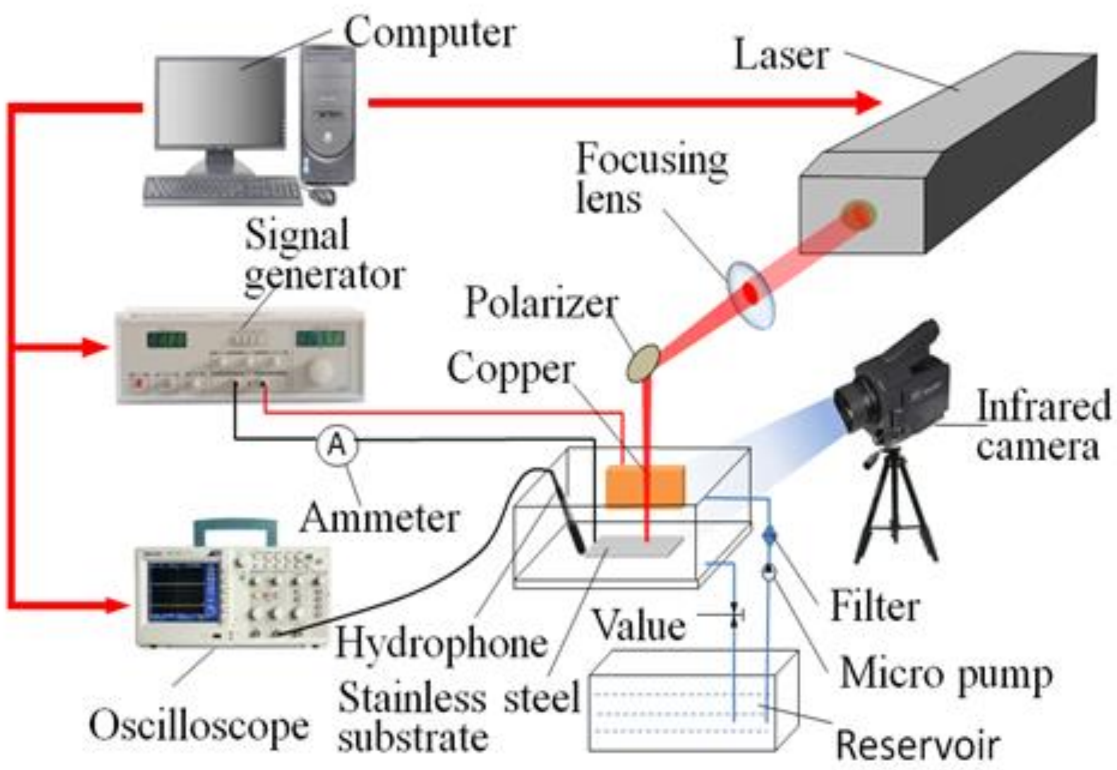

Figure 2. Diagram of the laser and electrodeposition composite processing system

The electrolyte solution absorbed the laser energy, resulting in an increase in the local temperature around the focus point An infrared camera was used to observe the change in temperature. When the energy density of the laser focus spot reaches the breakdown threshold of the solution, high-temperature and high-pressure plasma will be produced [11]. The adiabatic expansion of plasma leads to the formation of a plasma shockwave. The plasma shock wave spreads out a few millimeters at supersonic speed and then decays into a sound wave [12]. The pressure signal of the sound wave was measured by a hydrophone to determine the intensity of the plasma shock wave. The hydrophone was placed approximately 10 mm away from the laser focal point. As shown in fig. 2, the hydrophone was connected to an oscilloscope. The computer was used to analyze the waveforms detected by the oscilloscope.

2.2.3 Deposition rate and coating quality

To study the effect of laser irradiation on the deposition rate, the weight of the cathode substrate was measured before and after deposition using high-precision electronic scales. A scanning electron microscope (SEM) was used to observe the surface topography and the grains of the coating. An electronic universal testing machine (UTM4000 series) was used to test the tensile strength and ductility of the coating.

3. RESULTS AND DISCUSSION

3.1 Mechanical and thermal effects

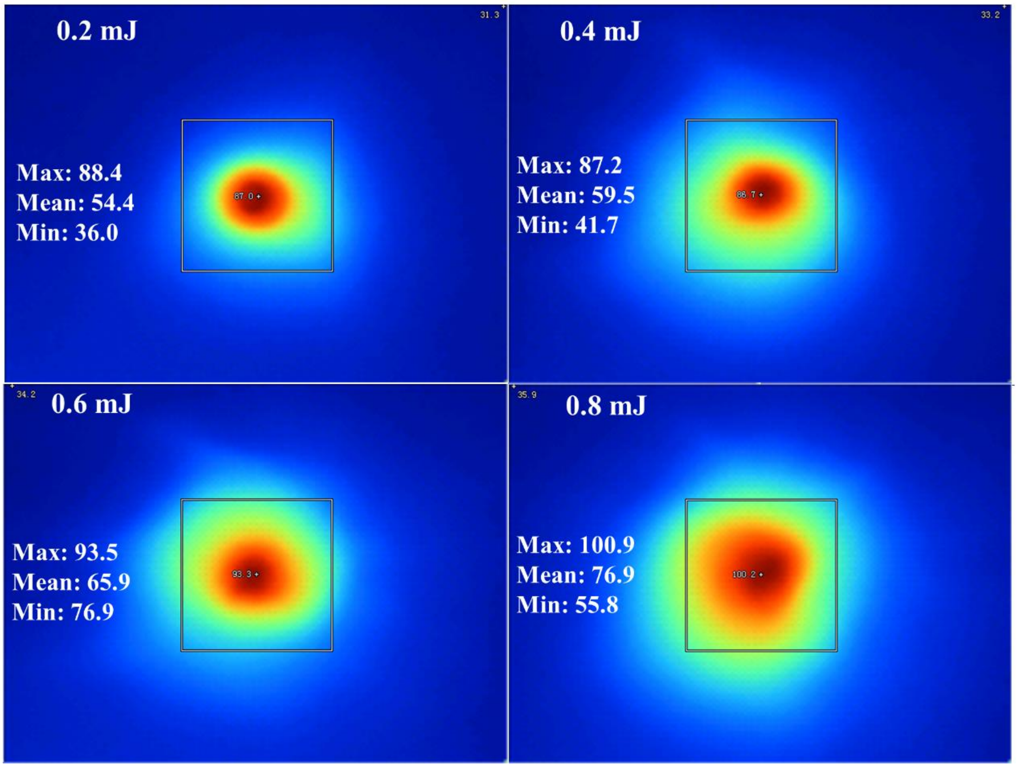

Figure 3. Diagram of the temperature gradients of the bath with varying laser energies

The temperature distribution images were taken with an infrared camera (Fluke-Ti-45) and are shown in Fig. 3. Since the electrolyte solution absorbed the laser energy, the temperature at the focus spot increased rapidly, and a gradient distribution appeared. The maximum temperature at the focus spot increased with the increase of the single-pulsed laser energy. Additionally, the heat affected area gradually expanded when the laser energy was increased. When the single-pulsed laser energy was 0.8 mJ, the temperature at the focus spot reached the boiling point of electrolyte solution, which caused the electrolyte solution to splash and halted the electrodeposition process.

The shockwave signals generated by lasers with varying single-pulsed energies are shown in fig. 4. The values measured for sound pressure indicate that the pressure increased with increasing single-pulsed laser energies. Since a large amount of energy is lost during propagation, the actual value for the plasma shockwave pressure is expected to be much larger.

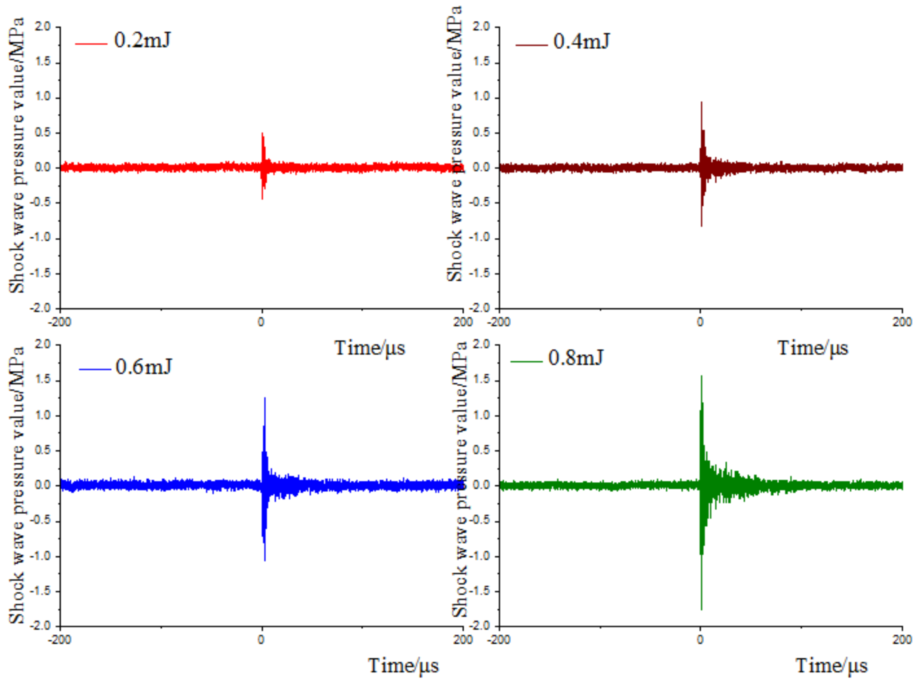

Figure 4. Shockwave signals with varying laser energies

3.2 Effect of laser irradiation on deposition rate

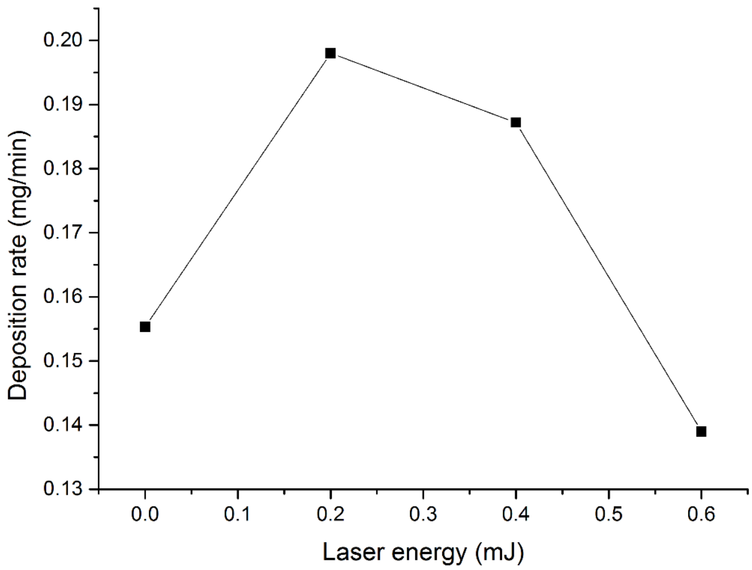

Figure 5. Relationship between single-pulsed laser energy and deposition rate

The influence of laser irradiation on the deposition rate is shown in fig. 5. The deposition rate was 0.155 mg/min without laser irradiation. When the single-pulsed laser energy was 0.2 mJ, the deposition rate was enhanced by 27.74%, and a large value of 0.198 mJ/min was achieved. However, the deposition rate decreased when the single-pulsed laser energy was further increased. When the single-pulsed laser energy was increased to 0.6 mJ, the deposition rate was only 0.139 mg/min, which is lower than the rate achieved without laser irradiation.

The machining currents with and without laser irradiation were record by a current probe to study the effect of laser irradiation on deposition rate. The current waves associated with electrodeposition compounded with laser irradiation of 0.4 mJ in energy and normal electrodeposition are shown in Fig. 6. The maximum current increases considerably during electrodeposition when laser irradiation is used.

Laser irradiation increases the local temperature of the electrolyte solution, which causes an increase in the rate of diffusion of the ions.

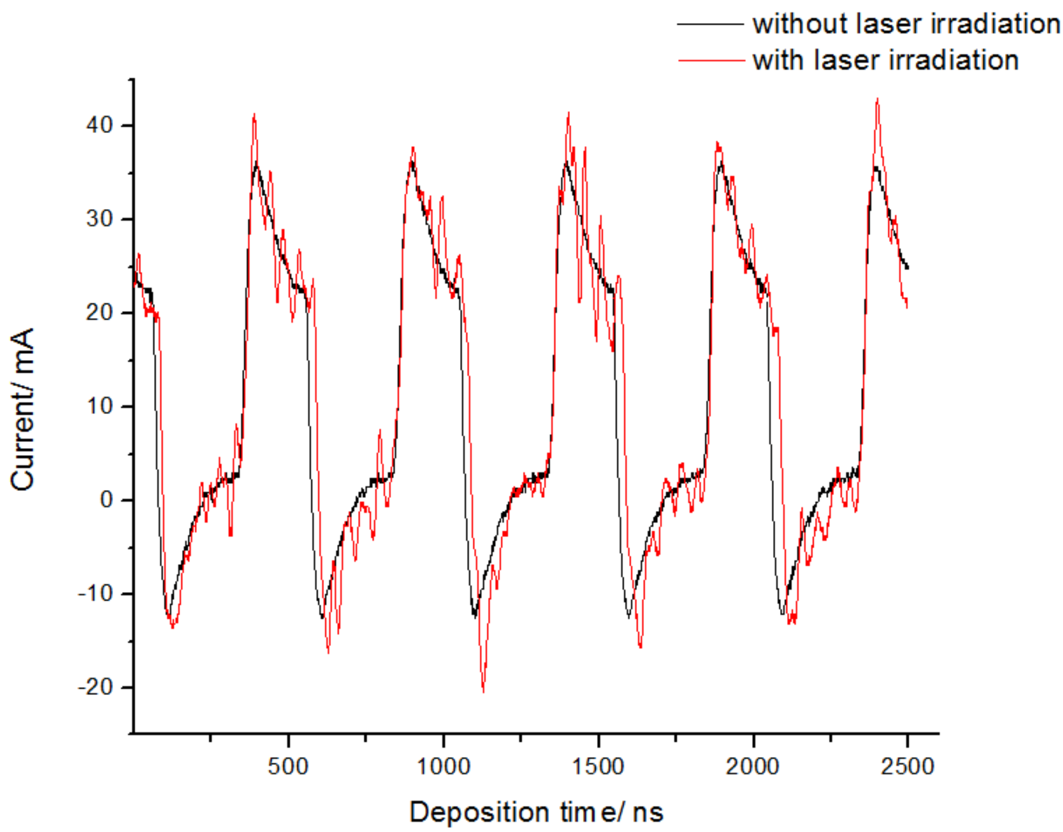

Figure 6. Deposition current with and without laser irradiation

The conductivity of the solution is related to the concentration of the solution and the rate of diffusion of the ions. An increase in the temperature of the solution leads to an increase in conductivity [13]. The increase in conductivity results in an enhanced current density. Therefore, the current density is closely related to the diffusion flux. According to the Stokes-Einstein equation,

$$D_i = kT\ /\ 6\pi r_i\eta \qquad (1)$$

where D_i is the diffusion coefficient, T is the absolute temperature, r_i is the effective particle radius, and η is the viscosity coefficient of the medium. In the process of electrodeposition, the current density is [14],

$$j = nF\ /\ v_i \cdot D_i \cdot (dc_i/dx) \qquad (2)$$

where j is the current density, n is the number of electrons in the reaction, F is Faraday's constant, v_i is the number of reactions of the ith particle, c_i is the ith particle concentration, x is the concentration polarization range, dc_i/dx is the concentration gradient of the solution, and dc_i/dx is the diffusion flux. According to Faraday's law [14],

$$j = nFv \qquad (3)$$

where v is the deposition rate. Therefore,

$$v = 1\ /\ v_i \cdot (kT/6\pi r_i\eta) \cdot (dc_i/dx) \qquad (4)$$

Hence, an increase in temperature results in an increase of the deposition rate. V.I. Grishko et al. also reported that the thermal effect of the laser leads to an enhancement of the electrode reaction rate [6]. Furthermore, the mechanical effect of the laser can also effectively alleviate concentration polarization phenomena during the deposition process. The mechanical effect of the laser is mainly attributed to the plasma shockwave and the collapse of cavitation bubbles. The liquid surrounding the high-temperature plasma absorbs the energy and evaporates to yield cavitation bubbles [11]. The plasma shockwave and the collapse of the cavitation bubbles generate micro agitations in the solution. This accelerates the mass transfer rate of the liquid phase and reduces the concentration polarization, which increases the reaction rate. When the single-pulsed laser energy is too large, however, the plasma shockwave will block the deposition process. The laser may even ablate the deposition layer and the cathode substrate. This is why the deposition rate is lower at a single-pulsed laser energy of 0.6 mJ than in the absence of laser irradiation.

3.3 Effect of laser irradiation on coating quality

3.3.1 Analysis of surface morphology

The SEM images of the coating are shown in fig. 7. Varying the single-pulsed laser energy resulted in a range of morphologies. The grain size decreased as the single-pulsed laser energy increased. At a single-pulsed laser energy of 0.2 mJ, the average grain size was only one-quarter of that which is produced by conventional electrodeposition, and Nano-scale grains were obtained with larger single-pulsed laser energies. The increase in the temperature of the local solution increases the over-potential of the cathode, which may enhance the nucleation rate. This leads to an increase in the number of the nucleation growth points and a reduction in the grain size.

The photoelectric field and the applied electric field have a direct effect on the direction of metal ion migration and dendrite growth [16]. Under the intermittent action of the pulsed laser and pulsed power supply, both the direction of the photoelectric field and that of the applied electric field exhibited similar changes. It was observed that the grains grew in a crisscross shape of granular and stripe morphologies, as shown in fig. 7 (c) and fig. 7 (d).

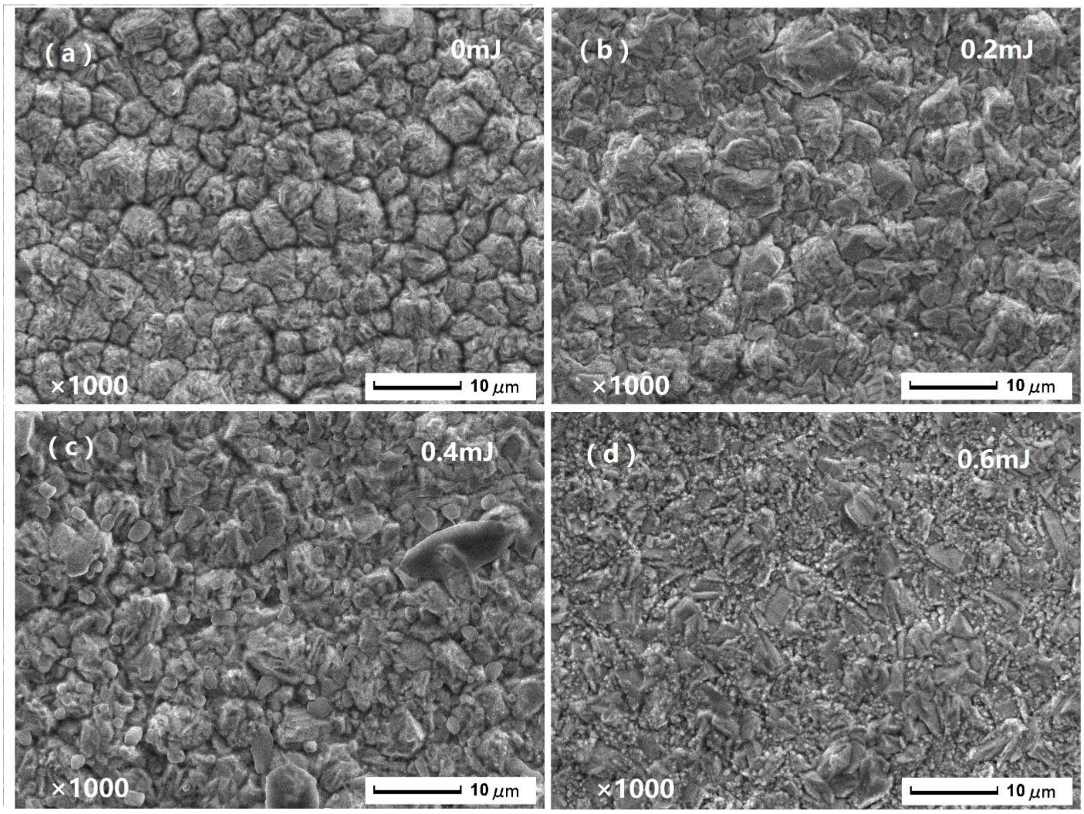

Figure 7. The surface topography images associated with deposition under varying laser energies

3.3.2 Tensile strength and ductility of the coating

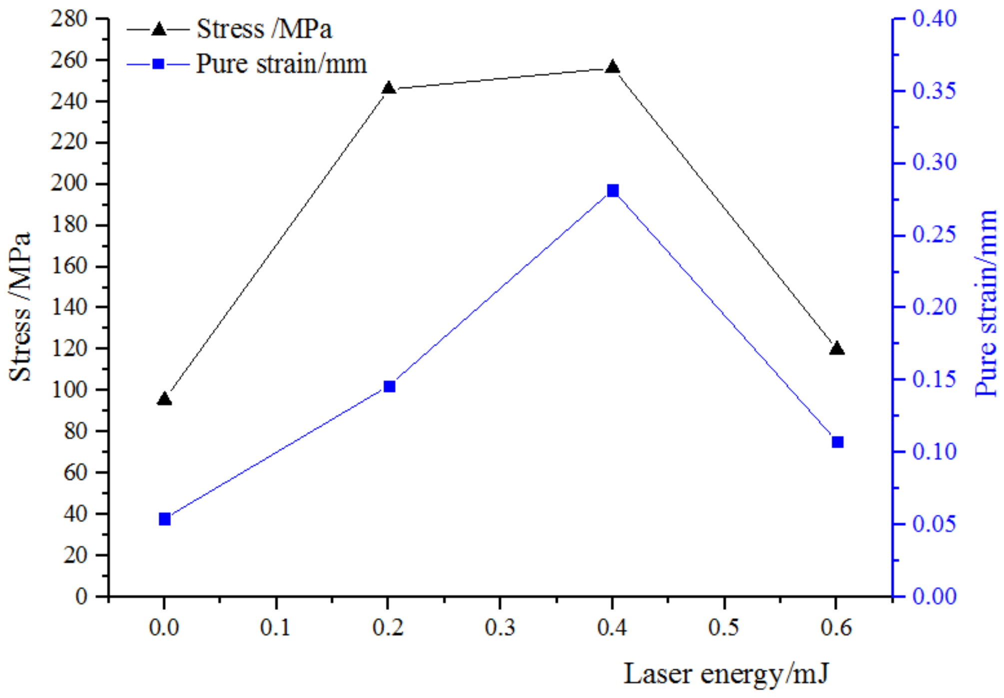

Figure 8. The relationship between the tensile strength, ductility and laser energy

The effect of laser irradiation on tensile strength and ductility was investigated by a tensile test. The tensile strength and ductility of the coating were improved by using laser irradiation, as shown in Fig. 8. When the single-pulsed laser energy was 0.4 mJ, the best tensile strength and ductility were achieved in the coating. When the single-pulsed laser energy was 0.6 mJ, the tensile strength and ductility of the coating began to decrease. This result is similar to what was discovered in the work on laser assisted electrodeposition of Cu_2ZnSnS_4 onto photovoltaic thin films by Qiong Nian et al [9].

The tensile strength and ductility of the coating are related to the grain size and the number of coating defects. When comparing Fig. 7 (a) and Fig. 7 (b), it is observed that the dislocation density increased and the grains bonded more strongly by using laser irradiation and that grain refinement helps to increase the tensile strength and ductility of the coating. In addition, the reduction of copper ions in the solution is accompanied by hydrogen evolution. The hydrogen bubbles generated adhere to the surface of the cathode substrate, and cause defects in the coating. [10] The plasma shockwave and the jet impact of the bubbles can remove the hydrogen bubbles from the surface to reduce the defects and improve the quality of coating. [17] However, if the plasma shockwave is too strong, additional defects such as micro cracks, pits and pinholes may increase.

4. CONCLUSION

In this work, laser irradiation with varying single-pulsed laser energies was introduced into an electrodeposition process. The mechanical and thermal effects of laser irradiation were investigated. Absorption of the laser energy by the solution resulted in an increase in the temperature near the focus spot. Laser irradiation induced the generation of high temperature and high pressure plasma. The expansion of the plasma compressed the electrolyte with sufficiently high pressure to form a plasma shock wave.

Increasing the temperature led to an increase in the electrical conductivity and the diffusion coefficient of the electrolyte solution. This contributed to an increase in the current density, such that the deposition rate increased. The plasma shockwave and collapse of cavitation bubbles generated micro agitations in the solution. This accelerated the liquid phase mass transfer rate and reduced the concentration polarization, which increased the reaction rate.

The increase in temperature can also increase the cathode over-potential, leading to grain refinement. Laser irradiation increased the dislocation density, resulting in a more compact coating. The plasma shockwave can remove hydrogen bubbles adhering to cathode substrate in time to reduce the defects and improve the quality of the coating. Therefore, the laser irradiation can increase the tensile strength and ductility of the coating.

If the single-pulsed laser energy is too large, it will inhibit normal deposition. The rate of deposition and the coating quality will both decline.

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