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Corrosion and Copper Foil Formation Behavior of Laser-Welded Joint and Spin-Formed Materials of Commercially Pure Titanium in $\text{H}_2\text{SO}_4/\text{CuSO}_4$ Electrolyte

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Abstract: Based on the microstructure characterization, electrochemical impedance spectroscopy, potentiodynamic polarization, and immersion corrosion, this work comparatively analyzed the differences in the electrochemical corrosion morphology and post-foil formation surface morphology of laser beam welded (LBW) sample and spin-formed sample, and compared the corrosion resistance and Cu foil formation ability of two samples in $\text{H}_2\text{SO}_4/\text{NaCl}$ solution and CuSO_4 reducing electrolyte. Results show that in H_2SO_4 and NaCl solutions, LBW sample and spin-formed sample exhibit excellent passivation ability and corrosion resistance. Both samples show uniform corrosion morphologies and similar corrosion resistance in the strong acidic solution containing Cl^- . Meanwhile, the Cu foil formation ability of the welded joint is similar to that of the spin-formed sample, and both samples obtain intact Cu foils with high-quality surfaces and small differences in properties.

Key words: Ti cathode; laser beam welding; spin forming; corrosion; Cu foil electroplating

1 Introduction

Cu foil is the key material for manufacturing electronic products such as lithium-ion batteries, Cu clad plates, and printed circuit boards^[1-4]. Among the various methods for manufacturing Cu foils, electroplated Cu foil is an efficient method that has been developed in recent years^[5-9]. At present, electroplated Cu foil is mainly fabricated using commercially pure Ti (CP-Ti) cathode drum, which is manufactured via spin forming^[10-11]. The spin-formed CP-Ti cathode drum has the advantages such as seamless, fine grain, and uniform microstructure. However, the process prior to pre-spin forming is very complicated. The CP-Ti billet needs to undergo at least the steps including punching, reaming, rolling ring, and then spin forming^[11], which causes high risk of cracking and processing cost. Moreover, the expenses of spin forming equipment and supporting molds are extremely high.

Compared with spin forming, the laser beam welding (LBW) method is an alternative method for manufacturing CP-Ti cathode drums by welding the bended CP-Ti plates, which has been proposed recently^[12]. It has the advantages of easier process, higher production efficiency, more flexible size, and lower cost. However, LBW method will inevitably bring microstructural and property differences of the cathode drum in the weld zone^[12-15], which remains to be major concerns that require extensive research.

Firstly, as the cathode material for preparing Cu foil, CP-Ti drums are continuously exposed to acidic plating solutions containing corrosive media such as H_2SO_4 , HCl , and NaCl , posing a risk of corrosion during service. Li et al^[18] analyzed the electrochemical corrosion behavior of high-frequency induction welded TA1 pure Ti thin-walled tubes in NaCl solution. They found that the welded joint has higher

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corrosion potential, larger polarization resistance, and lower corrosion rate. Zhang et al.^[19] reported that the welded joint of TA2 pure Ti, obtained through tungsten inert gas welding, is prone to stress corrosion and hydrogen embrittlement in HCl solution, with the weld zone being the weakest region. Wang et al.^[20] investigated the corrosion behavior of pure Ti tungsten inert gas welding joints in simulated desulfurization flue gas condensate media. They revealed that the corrosion resistance of the weld zone is very close to that of the base metal, and the surface protective film formed by oxidation during welding can enhance the corrosion resistance of the welded joint. Clearly, it is still controversial according to the previous reports regarding the corrosion resistance of the weld joint and base metal of pure Ti. Particularly, in the acidic Cu electroplating medium, the corrosion performance of LBW joint is obscure. Therefore, it is essential to investigate the corrosion performance to provide a critical reference for the safe service of CP-Ti cathode drums fabricated by LBW.

In addition, during the electroplating process for preparing Cu foil, different microstructures of LBW joint and spin-formed CP-Ti may affect the electrochemical processes such as surface passivation, charge transfer, and reduction reaction of Cu²⁺ ions^[21]. However, the previous research was mainly focused on the effect of additives on the electroplating electrolytes, such as hypophosphite^[22], gelatin^[23], and other inorganic or organic additives^[10]. Reports about the influences of grain structure and subgrain features on electrochemical processes are scarce^[21]. Therefore, a detailed analysis of the foil formation properties of LBW joint and a comprehensive comparison with spin-formed CP-Ti are necessary to provide theoretical basis for the application of LBW technology in CP-Ti cathode drums for the manufacturing of electroplated Cu foil.

In this work, the corrosion behavior and foil formation properties of CP-Ti LBW joint and spin-formed components were studied. The microstructures were observed via optical microscope (OM) and electron back-scattered diffraction (EBSD). Electrochemical impedance spectroscopy (EIS) and potentiodynamic polarization measurements were employed to analyze the electrochemical corrosion properties in H₂SO₄ and NaCl solution. Immersion corrosion morphology in acidic environment was characterized by scanning electron microscope (SEM). The early-stage growth behavior of Cu foil and the final stage morphologies were analyzed using OM and SEM. This research provides valuable guidance for the future application of LBW technology in the manufacturing of CP-Ti cathode drums for electroplating of Cu foil.

2 Experiment

The CP-Ti used in the present work is Grade 1 according to the ASTM Standard B265. It is at annealing state with the dimension of 150 mm×150 mm×6 mm, and the chemical composition is given in Table 1.

A YLS-4000 continuous fiber laser with a Motoman-NX100 six-axis welding robot was employed for the welding. LBW joint was prepared using a combination of penetration

Table 1 Chemical composition of CP-Ti (wt%)

Fe	N	C	H	O	Ti
0.016	0.003	0.010	0.0006	0.060	Bal.

laser welding and multi-layer/pass laser wire feeding. Based on our previous attempts, the optimized LBW parameters used in this work were as follows. (1) Penetration welding: laser power of 2200 W and welding speed of 80 cm·min⁻¹; (2) Wire feeding welding: laser power of 2500 W, welding speed of 50 cm·min⁻¹, and wire feeding rate of 430 cm·min⁻¹. During the welding process, the laser beam was inclined for 15°. Ar gas with the purity of 99.99vol% was used for the protection, and the gas flow rate was 25 L·min⁻¹. After welding, the sample was heat-treated at 580 °C for 1 h to optimize the microstructure in the weld zone.

For the spin forming processing, the original Ti roll with the wall thickness of 45 mm was heated at 500 °C for 2 h. The spinning deformation was 5 mm per pass, and the drum with a wall thickness of 25 mm was obtained, with the end spinning temperature of 260 °C. Finally, recrystallization annealing was performed at 500 – 550 °C for 1 h to acquire a fully recrystallized equiaxed grain structure.

Fig. 1 shows the microstructures of LBW and spin-formed CP-Ti samples observed via OM and EBSD. The kernel average misorientation (KAM) maps show the density of dislocations. The base metal of LBW sample is shown in Fig. 1a–1b, where the base metal is composed of uniform and equiaxed grains with the average size of 20 μm. Fig. 1c–1d indicate that the weld zone consists of finer equiaxed grains with the average size of 16 μm. However, it is clear that the size distribution of grains in the weld zone is wider than that in the base metal. Besides the grain size, it is found that the grains in the weld zone contain evident subgrain features, as shown by the red rectangle in Fig. 1c. Crisscross acicular α'-martensite phases exist in the grains of the weld zone due to the rapid solidification during welding, while no such feature is found in the base metal. As shown in Fig. 1e–1f, the spin-formed sample also consists of uniform and equiaxed grains with the average size of about 20 μm, and the subgrain feature of α' phase is not evident. It is clear from KAM maps that the spin-formed sample possesses much higher density of dislocations than other two samples. This is reasonable because of the severe deformation during spin forming.

Refer to the Cu electroplating electrolyte, this work chose the 120 g·L⁻¹ H₂SO₄ and 3.5wt% NaCl aqueous solution, and the electrochemical corrosion measurements were conducted at room temperature. A Corrtest CS370 electrochemical work station with a three-electrode system was utilized, where the reference electrode was Ag/AgCl (saturated KCl), the counter electrode was a Pt mesh, and the CP-Ti working electrode with an exposure area of 10 mm×10 mm was connected via Cu wire. The remaining surface of CP-Ti electrode was sealed with epoxy resin. Prior to the electrochemical measurements, the sample surface was ground with sandpaper

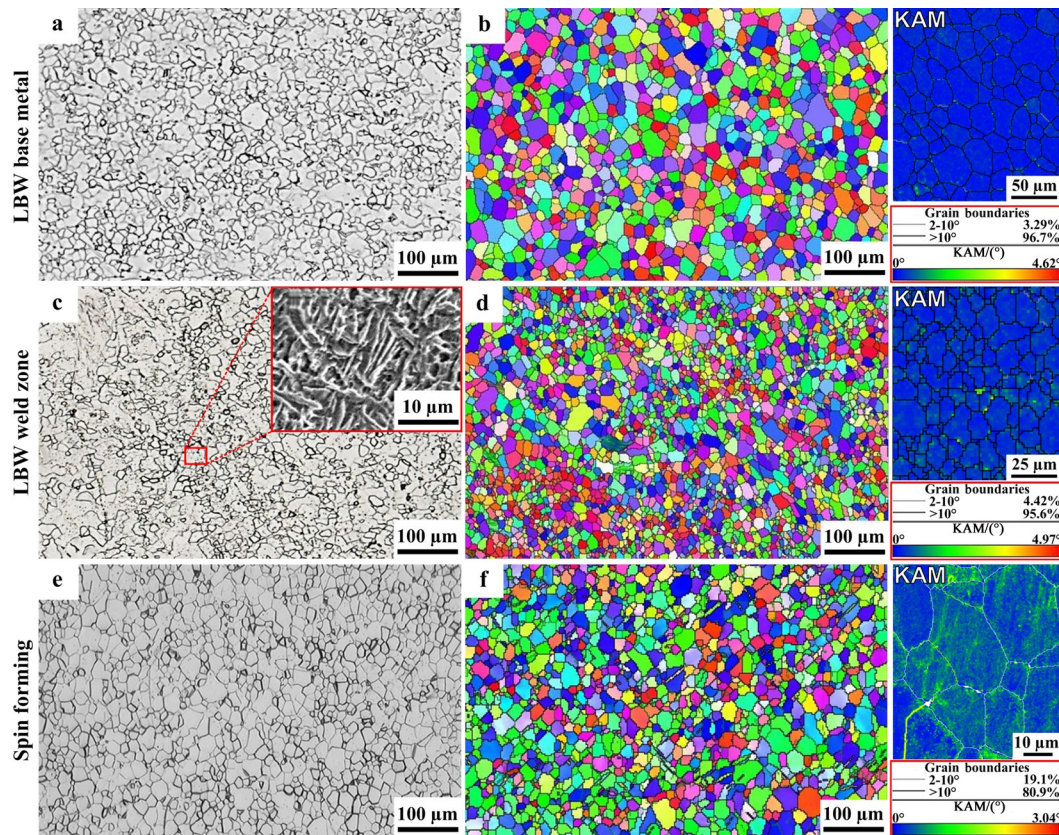


Fig.1 OM (a, c, e), EBSD-KAM (b, d, f) images of LBW base metal (a–b), LBW weld zone (c–d), and spin-formed sample (e–f)

up to 2000#, cleaned with ethanol, rinsed with deionized water, and then air-dried. After being held at the open circuit potential (OCP) in the solution for 2 h to stabilize the system, EIS test was conducted at OCP, with a frequency range of 10^5 Hz to 10^{-2} Hz and a perturbation potential of 10 mV. The potentiodynamic polarization curve started at -100 mV vs. OCP, scanned positively at a rate of $0.5 \text{ mV} \cdot \text{s}^{-1}$, and terminated when the anodic dissolution current density reached $1 \text{ mA} \cdot \text{cm}^{-2}$. All the electrochemical tests were repeated 3 times to ensure the reproducibility of the measurements.

The immersion corrosion test was carried out in an aqueous solution of $120 \text{ g} \cdot \text{L}^{-1} \text{H}_2\text{SO}_4 + 0.03 \text{ g} \cdot \text{L}^{-1} \text{HCl}$. Before the experiment, the sample surface was polished with the procedure the same as that for the CP-Ti working electrode. The immersion test was conducted at 50°C for 6 h, followed by rinsing with deionized water and ultrasonic cleaning with ethanol. The corrosion morphologies of LBW and spin-formed samples were observed using a Tescan Vega3 LMH type SEM.

The Cu electroplating experiments were conducted in saturated CuSO_4 aqueous solution. It should be noted that, to eliminate the possible influences from additives, sulfuric acid concentration, chloride ion concentration, and other experimental variables, only saturated CuSO_4 was applied in this study to ensure that the experimental results solely reflected the impact of material's microstructural differences on foil formation properties. The CP-Ti cathode electrode for electroplating had an exposure area of $10 \text{ mm} \times 20 \text{ mm}$, and it

was connected with Cu wire while the remaining surfaces were sealed with epoxy resin. Prior to electroplating, the sample surfaces were ground with sandpaper up to 8000#, cleaned with ethanol, rinsed with deionized water, and then air-dried. Based on preliminary research and parameter exploration, an electroplating current of $-100 \text{ mA} \cdot \text{cm}^{-2}$ was selected, with a foil formation time of 10 min, and the thickness of the Cu foil can reach about $15 \mu\text{m}$. After electroplating, the Cu foil was carefully removed with tweezers, rinsed with deionized water, and ultrasonically cleaned with ethanol. The surface morphologies of the Cu foils were observed using a Zeiss Axio Scope A1 type OM and a Tescan Vega3 LMH type SEM.

3 Results

3.1 Electrochemical corrosion performance

3.1.1 Electrochemical corrosion in H_2SO_4 solution

The EIS-Nyquist spectra of LBW joint and spin-formed samples in $120 \text{ g} \cdot \text{L}^{-1} \text{H}_2\text{SO}_4$ solution are shown in Fig.2. Both samples exhibit typical capacitive arc characteristics, indicating similar electrochemical corrosion behavior. To simplify the comparison, the one-time-constant resistor-capacitor circuit given in the inset in Fig.2 was used for the EIS fitting, and the results are presented in Table 2. Herein, R_s represents the solution resistance, n is the exponent ($0 < n \leq 1$) in the fitting of the constant phase element (CPE), R_{ct} is the charge transfer resistance, and C_{dl} is the double-layer

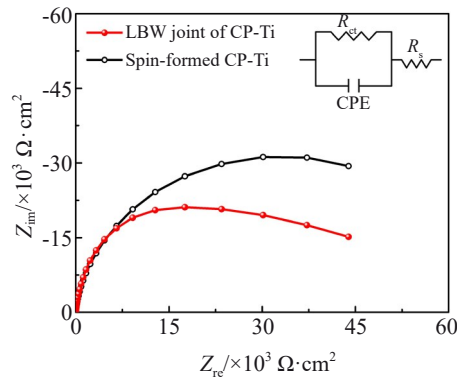


Fig.2 EIS-Nyquist spectra of LBW joint and spin-formed samples of CP-Ti in 120 g·L⁻¹ H₂SO₄ solution with equivalent electric circuit for fitting

Table 2 Fitting results of EIS data in Fig.2

Parameter	$R_s/\Omega\cdot\text{cm}^2$	n	$R_{ct}/\times 10^4\Omega\cdot\text{cm}^2$	$C_{dl}/\times 10^{-5}\text{F}\cdot\text{cm}^{-2}$
LBW joint of CP-Ti	1.26	0.94	4.61	1.51
Spin-formed CP-Ti	0.93	0.93	6.98	1.48

capacitance. Generally, the R_{ct} reflects the corrosion resistance of the system, and higher R_{ct} indicates better corrosion resistance of the sample. As shown in Table 2, the R_{ct} values of both samples are close to $10^5\Omega\cdot\text{cm}^2$, indicating the excellent corrosion resistance. Specifically, the R_{ct} of LBW joint is slightly smaller than that of the spin-formed sample, suggesting that LBW joint exhibits slightly lower corrosion resistance. Furthermore, the close values of CPE exponent (n) and C_{dl} for both samples also reflect their minimal differences in corrosion resistance.

Fig. 3 depicts the potentiodynamic polarization curves of LBW joint and spin-formed samples in 120 g·L⁻¹ H₂SO₄ solution. It can be seen that CP-Ti exhibits weak passivation ability in this H₂SO₄ solution, and the current density rises with the continuous increase in potential in the anodic region. The curves of both samples are very close, indicating the similar electrochemical corrosion behavior. The Tafel fitting method was applied to fit the polarization curves, and the

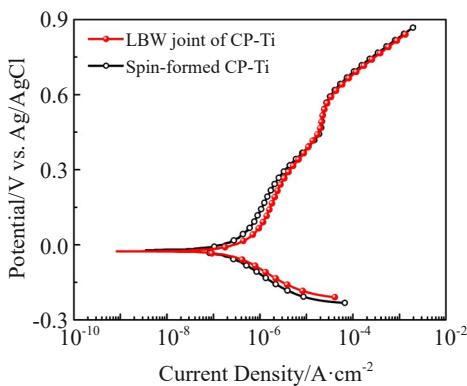


Fig.3 Potentiodynamic polarization curves of LBW joint and spin-formed samples of CP-Ti in 120 g·L⁻¹ H₂SO₄ solution

results are shown in Table 3. The corrosion potential (E_{corr}) reflects the thermodynamic tendency of corrosion, with a more positive value indicating a lower tendency for corrosion^[24]. The corrosion current density (j_{corr}) characterizes the corrosion rate, and a smaller value indicates a slower corrosion rate^[25]. The film breakdown potential (E_{bd}) reflects the stability of the passivation film, with a more positive value indicating better stability and stronger resistance to high-potential breakdown of the passive film^[26]. ΔE represents the width of the passivation region ($\Delta E=E_{bd}-E_{corr}$), and a wider passivation region indicates better stability of the passivation film. As shown in Table 3, LBW joint sample exhibits a more negative E_{corr} , a lower E_{bd} , and a narrower passivation region width. However, the overall potential differences of two samples are within the range of 5–33 mV, indicating that the corrosion resistance of the welded joint is slightly lower than that of the spin-formed sample. The j_{corr} of two samples are in the order of $10^{-7}\text{A}\cdot\text{cm}^{-2}$, suggesting good corrosion resistance for both samples, and the corrosion rate of the welded joint is slightly higher than that of the spin-formed sample. Clearly, the polarization results are in good agreement with that of the EIS measurements.

3.1.2 Electrochemical corrosion in NaCl solution

During the Cu electroplating process, NaCl is often added to the electroplating solution to enhance the uniformity and compactness of the coating and improve the plating efficiency^[27–28]. Therefore, this work compares the electrochemical corrosion performances of LBW joint and spin-formed samples in the 3.5wt% NaCl aqueous solution. Fig. 4 shows the EIS-Nyquist spectra of two samples. Both samples exhibit capacitive arc characteristics, and the welded joint sample displays a larger capacitive arc radius, indicating superior corrosion resistance in Cl⁻ medium. EIS spectra are fitted using the equivalent electric circuit as shown by the inset in Fig.4, and the results are presented in Table 4. The R_{ct} of the welded joint sample is $4.21\times 10^5\Omega\cdot\text{cm}^2$, which is approximately three times larger than that of the spin-formed sample, indicating that the welded joint possesses stronger corrosion resistance in the aggressive Cl⁻ environment. Since the C_{dl} is inversely proportional to the thickness of passivation film, the lower C_{dl} value for the welded joint sample suggests a thicker passivation film, offering better protection for the CP-Ti substrate. Notably, compared to the 120 g·L⁻¹ H₂SO₄ solution, the R_{ct} values of both samples in the NaCl solution increase by an order of magnitude. This is because the passivation film of CP-Ti consists primarily of oxides such as TiO₂ and Ti₂O₃^[29–30]. In strong acidic solutions, the dissolution effect on the passivation film is more pronounced, resulting in a thinner film and reduced protection to the substrate. In

Table 3 Tafel fitting results of polarization curves in Fig.3

Parameter	$E_{corr}/\text{V vs. Ag/AgCl}$	$j_{corr}/\times 10^{-7}\text{A}\cdot\text{cm}^{-2}$	$E_{bd}/\text{V vs. Ag/AgCl}$	$\Delta E_{pass}/\text{V}$
LBW joint of CP-Ti	-0.026	4.15	0.585	0.611
Spin-formed CP-Ti	-0.021	2.72	0.618	0.639

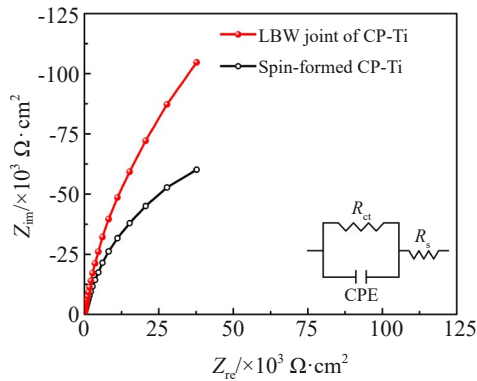


Fig.4 EIS-Nyquist spectra of LBW joint and spin-formed samples of CP-Ti in 3.5wt% NaCl solution with equivalent electric circuit for fitting

Table 4 Fitting results of EIS data in Fig.4

Parameter	$R_s/\Omega \cdot \text{cm}^2$	n	$R_{ct}/\times 10^5 \Omega \cdot \text{cm}^2$	$C_{dl}/\times 10^{-5} \text{F} \cdot \text{cm}^{-2}$
LBW joint of CP-Ti	1.76	0.87	4.21	1.02
Spin-formed CP-Ti	1.68	0.86	1.47	1.30

contrast, in the neutral Cl^- environment, Cl^- primarily attacks oxygen vacancies on the surface of the passivation film^[31], inducing the Schottky-pair reaction which increases the point defect density within the film, thereby enhancing the cation flux inside the film and leading to a lower protection capability of the film. However, there is no doubt that the thinning effect of Cl^- is less significant than that of concentrated acidic solution. This is the fundamental reason for the larger capacitive arc in Fig.4 than that in Fig.2.

The electrochemical corrosion properties of two samples in 3.5wt% NaCl solution were measured using the potentiodynamic polarization method, and the results are shown in Fig. 5, with the fitting data presented in Table 5. Compared with acidic solution (Fig. 3), both samples exhibit wider passivation regions in the NaCl solution, indicating stronger protective effects of the passivation film. Compared with the spin-formed sample, the welded joint sample has slightly lower E_{corr} and E_{bd} , but a wider passive range. However, for the passivation region as wide as about 1.3 V, the difference of 0.081 V in the width of passive range is not significant. The j_{corr} of the welded joint sample is $2.13 \times 10^{-8} \text{A} \cdot \text{cm}^{-2}$, while that for the spin-formed sample is $7.62 \times 10^{-8} \text{A} \cdot \text{cm}^{-2}$, suggesting that the welded joint exhibits a slightly slower corrosion rate than the spin-formed sample. Clearly, the samples exhibit better corrosion resistance in NaCl solution than in H_2SO_4 solution (j_{corr} is about $10^{-7} \text{A} \cdot \text{cm}^{-2}$), agreeing well with the trend reflected by EIS data. For the anodic branches in the passivation region, the curves of both samples almost completely overlap, indicating similar protective effects from the passivation films. In addition, the polarization curve of LBW joint sample has an increased current peak in the potential range of

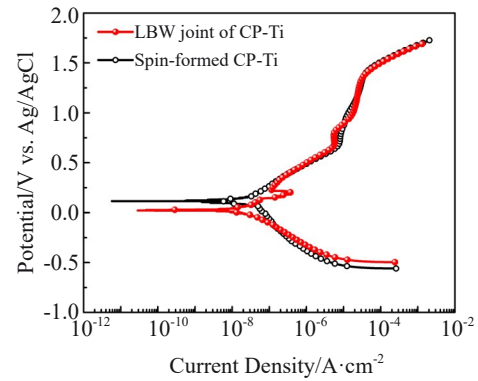


Fig.5 Potentiodynamic polarization curves of LBW joint and spin-formed samples of CP-Ti in 3.5wt% NaCl solution

Table 5 Tafel fitting results of polarization curves in Fig.5

Parameter	$E_{\text{corr}}/\text{V vs. Ag/AgCl}$	$j_{\text{corr}}/\times 10^{-8} \text{A} \cdot \text{cm}^{-2}$	$E_{\text{bd}}/\text{V vs. Ag/AgCl}$	$\Delta E_{\text{pass}}/\text{V}$
LBW joint of CP-Ti	0.020	2.13	1.409	1.389
Spin formed CP-Ti	0.115	7.62	1.423	1.308

0.14–0.21 V vs. Ag/AgCl, which is a typical metastable pitting feature. The occurrence of metastable pitting phenomenon is quite normal for passive alloys in NaCl solution, particularly when the passive film is not well grown on the alloy surface in the active-to-passive transition region, although this transition is not very distinct for CP-Ti under the present corrosion condition.

3.1.3 Immersion corrosion

During the electroplating process, which includes steps such as equipment preparation, intermittent inspections, and shutdowns, the CP-Ti cathode drum is actually in a naturally immersed state. With regard to such situations, it is necessary to investigate the immersion corrosion resistance of LBW and spin-formed CP-Ti to provide important reference for the safe operation of the cathode drum.

As mentioned earlier, the primary corrosive agents in the electroplating solution are H_2SO_4 and Cl^- ions. Therefore, the immersion test was conducted in an aqueous solution of $120 \text{g} \cdot \text{L}^{-1} \text{H}_2\text{SO}_4 + 0.03 \text{g} \cdot \text{L}^{-1} \text{HCl}$. After immersion at 50°C for 6 h, the corrosion morphologies of the welded joint (including the weld zone, heat-affected zone, and base metal) and spin-formed samples were observed, as shown in Fig. 6. For the welded zone in Fig. 6a, after immersion for 6 h, the surface exhibits typical characteristics of uniform corrosion, and reveals crisscross acicular α' -martensitic phases. According to the previous study, the formation of α' -martensite is due to the shearing lattice reconstruction of β -Ti under the high cooling rate in the molten pool during LBW^[32–34]. After immersion for 6 h, the surface layer of the weld zone is uniformly dissolved, without evident signs of localized corrosion such as pitting or intergranular corrosion. Fig. 6b–6c show the morphologies of the heat-affected zone and base metal after immersion corrosion, respectively. The corrosion morphologies of these

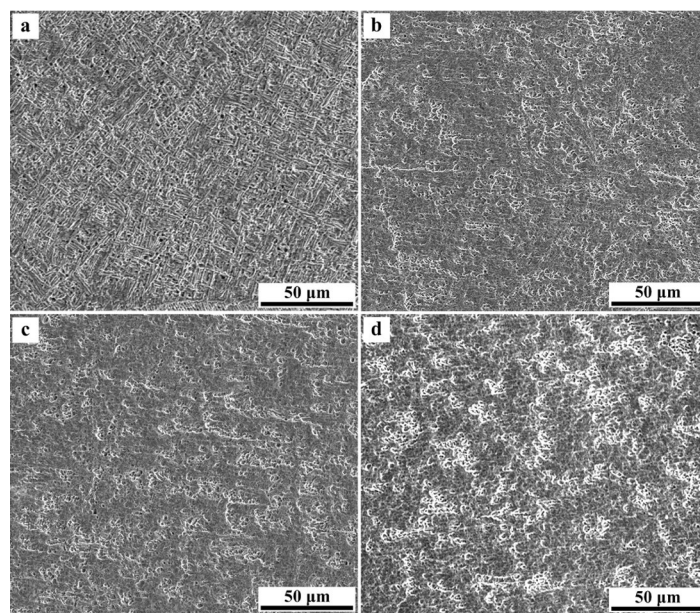


Fig.6 Corrosion morphologies of LBW weld zone (a), LBW heat-affected zone (b), LBW base metal (c), and spin-formed sample (d) after immersion in $120 \text{ g} \cdot \text{L}^{-1} \text{H}_2\text{SO}_4 + 0.03 \text{ g} \cdot \text{L}^{-1} \text{HCl}$ solution at 50°C for 6 h

two regions are very similar, both exhibiting quasi-uniform corrosion with abundant shallow pits distributed along the rolling direction (the horizontal direction). In general, the corrosion degrees of the heat-affected zone and base metal are similar to that of the weld zone. Fig.6d presents the corrosion morphology of the spin-formed sample, the shallow pits are arranged in bands along the spinning direction (the horizontal direction), and the corrosion feature is nearly identical to that of the heat-affected zone and base metal.

The immersion corrosion results in Fig.6 indicate that both LBW joint and spin-formed sample exhibit uniform corrosion morphologies and similar corrosion resistance in the strong acidic electroplating solution containing Cl^- , which is consistent with the similar corrosion resistance observed through electrochemical corrosion tests. Based on the electrochemical and immersion corrosion results, it can be concluded that LBW CP-Ti cathode drum material has excellent corrosion resistance in electroplating solution and can be applied to replace the spin-formed CP-Ti cathode drum from the perspective of corrosion performance.

3.2 Cu foil formation properties

3.2.1 Early-stage growth behavior

The early-stage growth behavior of Cu foil on the surfaces of CP-Ti LBW joint and spin-formed samples was compared using the electroplating method. Based on the experiment, SEM images of the deposited Cu with the electroplating duration of 5, 30, and 60 s were selected, as presented in Fig.7.

When the electroplating duration is 5 s, as shown in Fig.7a, 7d, and 7g, the surfaces of LBW weld zone, LBW base metal, and spin-formed samples are decorated with Cu particles. The weld zone and base metal of welded joint sample display similar Cu particle morphologies, and their Cu particles are finer and more dispersed than those of the spin-formed

sample. As shown in Fig.7b, 7e and 7h, after electroplating for 30 s, the Cu particles grow significantly, and continuous Cu bands are formed due to the collision and coalescence of the small particles. The morphologies of deposited Cu in three regions are similar, whereas the spin-formed sample has wider Cu bands which are interspersed with discontinuous Cu particles. Further extending the electroplating duration to 60 s, as depicted in Fig.7c, 7f and 7i, the Cu particles grow even larger and almost completely cover the surfaces of samples. The coverage of the Cu particles as a function of electroplating time was obtained through image analysis, and the results are given in Table 6.

It is clear that the coverage degree of different samples lies in the order of weld zone > base metal > spin-formed sample in the early stage of Cu foil growth. The early-stage growth characteristics indicate that the Cu foil formation ability of the weld zone is similar to that of the CP-Ti base metal and spin-formed sample, and it can be seen that the early-stage deposited Cu in the weld zone is more uniform and denser.

3.2.2 Surface morphologies of Cu foils

In the electroplated Cu foil field, the deposited Cu foil contains two sides: the rough side facing the electroplating solution and the smooth side facing the CP-Ti cathode. The morphologies of LBW joint and spin-formed samples on the rough sides are shown in Fig.8. Specifically, Fig.8a depicts OM image of LBW joint sample. Fig.8b and 8c show SEM images of the Cu foil on the weld zone and base metal surfaces, respectively. Fig.8d and 8e present OM and SEM morphologies of the Cu foil on the spin-formed sample, respectively. From a macroscopic perspective, the Cu foils are intact, dense, and flat. The quality of the rough sides for two samples is identical. SEM images suggest that the rough sides of the Cu foils are very dense, with abundant and uniformly

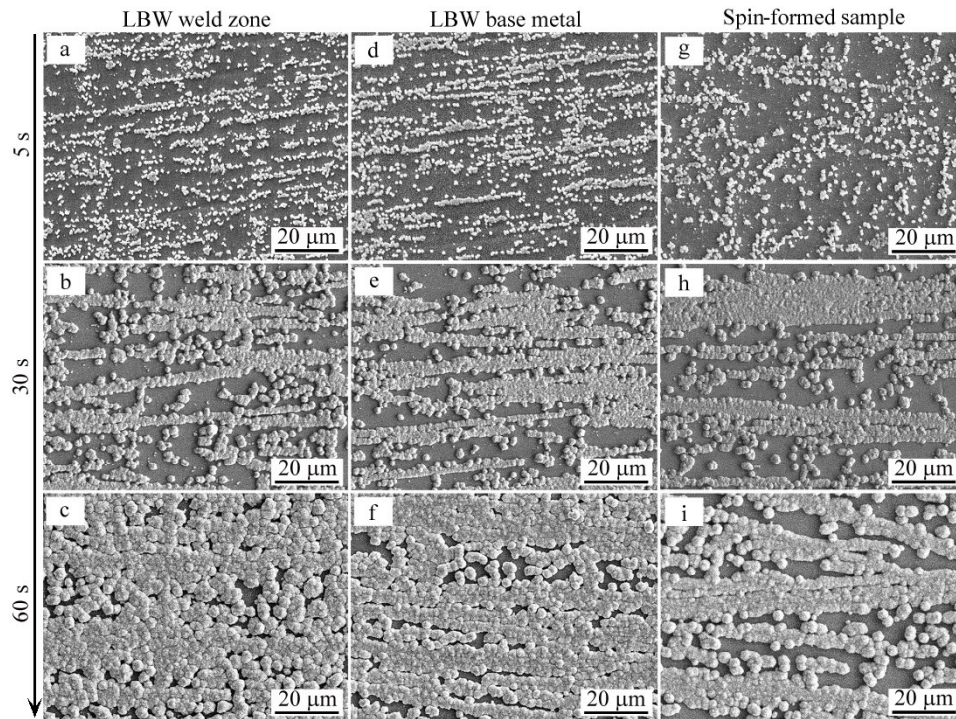


Fig.7 Early-stage surface morphologies of electroplating deposited Cu on LBW weld zone, LBW base metal, and spin-formed sample

Table 6 Coverage degree of Cu particles in Fig.7

Electroplating time/s	Weld zone/%	Base metal/%	Spin forming/%
5	25.8	24.6	20.2
30	45.5	44.0	43.7
60	83.5	76.1	59.4

distributed tiny humps, indicating that the Cu foils of both samples have good quality.

The morphologies of the Cu foils on smooth side are shown in Fig. 9. It should be noted that since the sample surfaces were polished by 8000# sandpaper, the smooth sides of the Cu foils replicate the surface topography of the samples, and thereby small scratches exist on the smooth sides. Fig. 9a presents OM morphology of LBW joint sample on the smooth side, Fig. 9b and 9c show SEM images of the Cu foil on the weld zone and base metal surfaces, respectively. As can be seen from the OM images, the smooth side in contact with the weld zone surface is slightly brighter. However, SEM images reveal that the smooth sides are intact, and there is no difference in the microscopic morphologies between the base metal and weld zone of LBW joint. Fig. 9d and 9e are OM and SEM images of the smooth side for the spin-formed sample, respectively. It is clear that the quality of the smooth side in contact with the spin-formed sample is similar to that of LBW joint, indicating that the Cu electroplating performance of LBW joint and spin-formed samples is nearly identical.

4 Discussion

4.1 Analysis of corrosion mechanism

The corrosion performance of CP-Ti LBW joint and spin-formed samples reveals that the spin-formed sample exhibits slightly higher corrosion resistance in H_2SO_4 solution, while the welded joint shows superior corrosion resistance in NaCl solution. Additionally, both samples display good passivation ability in H_2SO_4 solution and NaCl solution, with a relatively stronger passivation in NaCl solution than in H_2SO_4 solution. Then, the corrosion mechanisms of welded joint and spin-formed samples in these two solutions are discussed, with the schematic diagram in Fig.10.

(1) Weaker passivation ability in H_2SO_4 solution

CP-Ti is a typical passive metal, and it is well accepted that in liquid media, oxygen ions from H_2O , H_2SO_4 , as well as the dissolved O_2 in water can all promote the formation of oxide passive film. The passive film on the surface of pure Ti primarily consists of TiO_2 , with minor amounts of oxides such as Ti_2O_3 and TiO existing in the inner layer due to decreased oxygen activity^[37-39]. Considering the dissolution effect of H^+ on the outer barrier layer of the passive film in an acidic and chloride-free environment, the dissolution behavior of TiO_2 is focused in this research.

Due to the high density of point defects within the passive film, based on the point defect model (PDM)^[31,38], the following dissolution reactions occur at the film/liquid interface:



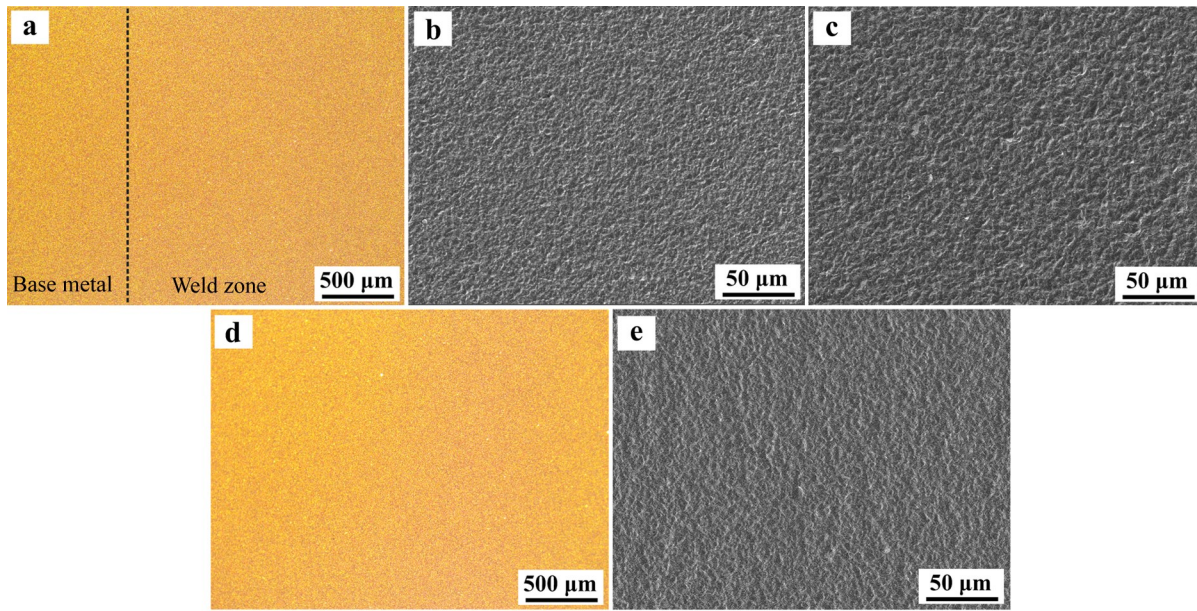


Fig.8 OM images (a, d) and SEM images (b–c, e) of Cu foils on rough sides of different samples: (a) LBW joint; (b) LBW weld zone; (c) LBW base metal; (d–e) spin-formed sample

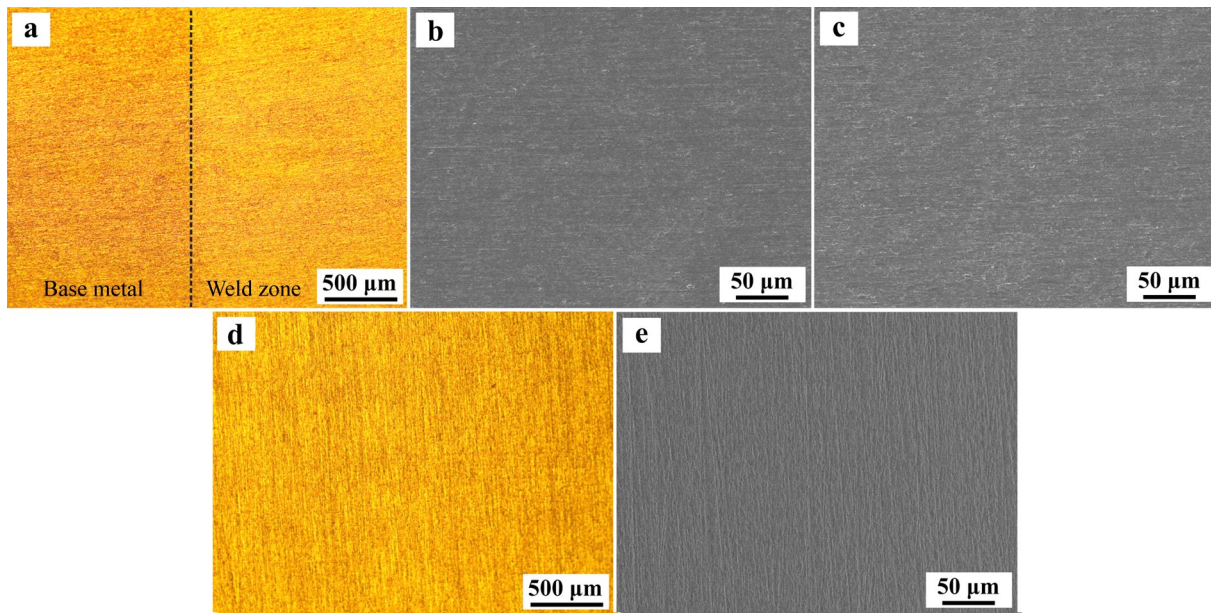


Fig.9 OM images (a, d) and SEM images (b–c, e) of Cu foils on smooth sides of different samples: (a) LBW joint; (b) LBW weld zone; (c) LBW base metal; (d–e) spin-formed sample

where Ti_{Ti} represents the Ti cation occupying lattice sites in the TiO_2 crystal, V_{Ti}^{4-} denotes the Ti vacancy formed after Ti dissolution, and Ti_{int} is the Ti cation located in the interstitial positions. When the solution contains a high concentration of H^+ , i.e., $120\text{ g}\cdot\text{L}^{-1}$ H_2SO_4 in this work, the dissolution reaction in Eq. (1) is significantly accelerated. In contrast, in NaCl solution, Cl^- ions are mainly inserted into the oxygen vacancies on the film surface, inducing localized ions flux inside the passive film, but hardly affecting the film thickness^[39]. Therefore, the passive film of CP-Ti in H_2SO_4 solution is thinner than that in neutral NaCl solution, as shown

in Fig.10.

(2) Corrosion mechanisms of LBW joint and spin-formed CP-Ti in H_2SO_4 solution

The dissolution reactions described in Eq. (2–3) lead to an increase in the concentration of V_{Ti}^{4-} and a decrease in the concentration of Ti_{int} on the film surface. Consequently, driven by concentration gradients and electric fields, V_{Ti}^{4-} diffuses inward from the surface into the metal/film interface, while Ti_{int} diffuses outward from the interior to the surface. This results in cation and anion fluxes within the passive film, as indicated by the tiny green arrows in Fig.10.

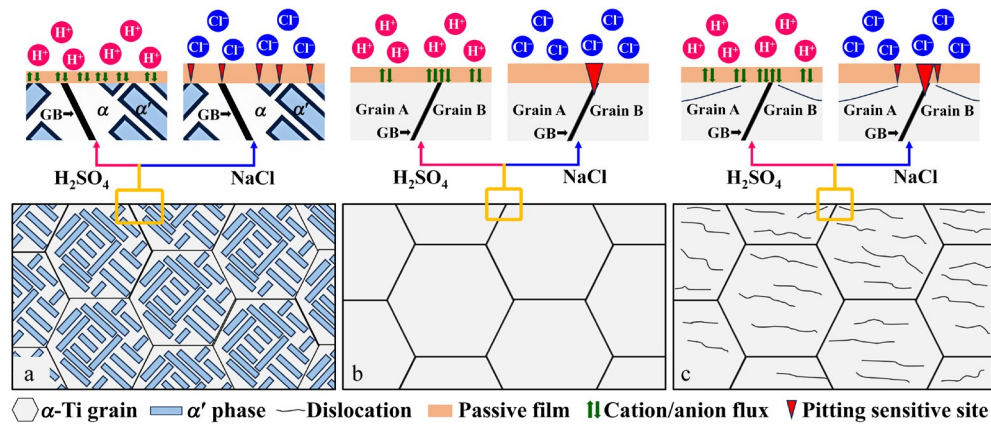


Fig.10 Schematic diagrams of corrosion mechanism in LBW weld zone (a), LBW base metal (b), and spin-formed sample (c) in H_2SO_4 and NaCl solutions (GB stands for grain boundary)

Previous microstructural analyses indicate that LBW joint consists of α -Ti grains with fine α' -martensite phases inside, while the base metal contains larger α -Ti grains, as depicted in Fig. 10a–10b. The spin-formed sample is also composed of α -Ti grains, but with a higher density of dislocations due to the severe deformation during spin forming. In acidic solution, the presence of α' -phases leads to the electrochemical activity difference between α and α' phases^[44]. The dispersed distribution of α' phases results in the even corrosion susceptibilities at α/α' phases interfaces and grain boundaries, increasing the ion diffusion fluxes within the passive film (Fig. 10a), and causing relatively uniform corrosion resistance of the weld zone. One direct evidence is shown in Fig. 6a, where the weld zone is uniformly corroded and the grain boundaries can hardly be seen, indicating that the grain boundary and α/α' interface have similar corrosion sensitivity.

For the base metal (Fig. 10b), the passive film above the α -Ti grains exhibits slow ion diffusion flux, but the grain boundaries offer a greater concentration of point defects, leading to the higher ions flux at these sites. As a result, the base metal has slightly higher corrosion resistance than the weld zone, but the base metal is more susceptible to pitting corrosion, as evidenced by the immersion corrosion results.

In Fig. 10c, the dislocations inside the grains of the spin-formed sample contribute to the elevated ions flux in the passive film. However, the overall passivation behavior of the spin-formed sample is similar to that of the base metal, making the spin-formed sample has slightly higher corrosion resistance than the weld zone.

(3) Corrosion mechanisms of LBW and spin-formed CP-Ti in NaCl solution

Compared with H_2SO_4 solution, the presence of Cl^- leads to different corrosion mechanisms regarding the deterioration of the passive film. When Cl^- ions are presented in the solution, they are inserted into the outermost oxygen vacancies ($\text{V}_\text{O}^\bullet$) of Ti oxide film, and trigger the Schottky-pair reaction^[39]:



The insertion of Cl^- into oxygen vacancies leads to the

increase in the concentration of V_Ti^{4-} on the surface of the oxide layer, which then diffuses to the metal/film interface due to the concentration gradient. If there are microstructural defects at the metal/film interface which hinder the annihilation of the V_Ti^{4-} point defects, the cumulative effect of V_Ti^{4-} intensifies, leading to the formation of voids^[41]. Consequently, breakdown of the passive film is more likely to occur at such locations, making them sensitive sites for pitting corrosion. Based on this framework, the effects of Cl^- and microstructural characteristics on the corrosion behavior are discussed.

As shown in Fig. 10a, in Cl^- environment, the sensitive sites of pitting corrosion in the weld zone are the α/α' phases boundaries and grain boundaries. Due to the dispersed distribution of the α' phase, both the α/α' phase boundaries and grain boundaries exhibit uniform activity. The small red triangles in Fig. 10a represent a large number of dispersed areas on the sample surface with relatively low sensitivity to pitting corrosion. In Fig. 10b, the base metal only consists of α grains, where the pitting is mainly concentrated at the grain boundaries. The larger red triangles above the grain boundaries represent the sensitive sites for pitting corrosion (Fig. 10b). Once the film breakdown takes place at the grain boundaries, the surrounding grains act as cathodes, resulting in localized dissolution under the effect of large cathode vs. small anode, which rapidly induces pitting corrosion. Therefore, the base metal has slightly higher pitting sensitivity than the weld zone. The corrosion behavior of spin-formed sample in Fig. 10c is similar to that of the base metal, while the difference is the dislocation sites which also enhance the pitting sensitivity. Therefore, it is concluded that in Cl^- environment, the weld zone exhibits superior corrosion resistance due to the tiny dispersed pitting-sensitive sites that lower the sensitivity of pitting corrosion.

4.2 Analysis of Cu foil growth mechanism

The analyses of Cu foil growth behavior of LBW and spin-formed samples reveal that during the early stage of Cu foil growth, the foil on the weld zone exhibits better uniformity and compactness. The foil growth mechanism

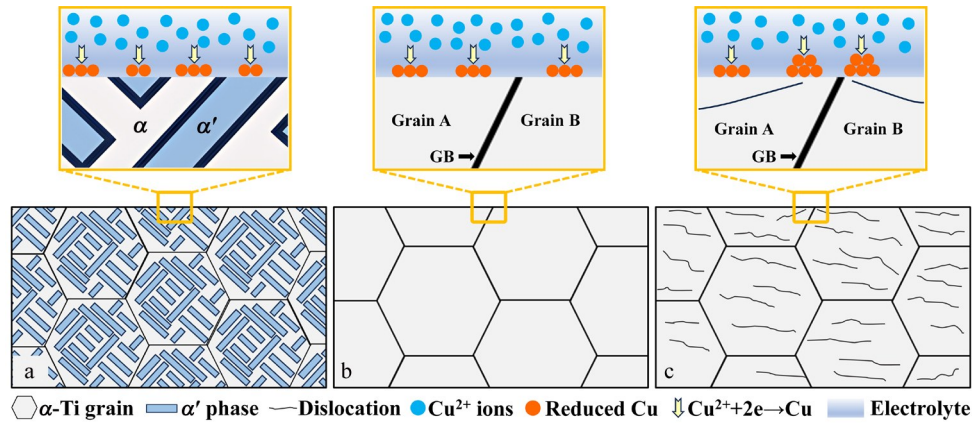


Fig.11 Schematic diagrams of Cu foil growth mechanism on the surfaces of LBW weld zone (a), LBW base metal (b), and spin forming sample (c)

of LBW and spin-formed samples will be discussed, as shown in Fig.11.

Because the cathodic reduction of Cu^{2+} inhibits the formation of passive film on the CP-Ti cathode surface, the Cu foil directly grows on the surface of CP-Ti substrate via the following reactions^[40]:



Cu foil growth requires rapid electron transport from the metal interior to the surface for the rapid electron consumption of Eq. (5 – 6). Hence, the lower electrical conductivities at grain and phase boundaries render these sites less prone to preferential nucleation. In addition, the process of Cu^{2+} adsorption, reduction of $\text{Cu}^{2+}/\text{Cu}^+$, and Cu deposition at the cathode surface have to cross the energy barriers^[21]. Thereby, it is understandable that different phase structures (α/α')^[34] and local defects (dislocations)^[41] on the metal surface promote Cu deposition.

Fig.11a illustrates that both the α and α' phases in the weld zone serve as the preferential sites for Cu deposition. Because the crystal structure of α' phase is similar to that of α phase, the Cu foil nucleates in the dispersed manner, leading to a more uniform growth. In Fig.11b, the Cu foil of base metal is preferentially nucleated on the surface of α grains. However, for the spin-formed sample, as shown in Fig.11c, in addition to nucleation of Cu deposits on the surface of α grains, dislocation can also reduce the energy barrier for Cu deposition^[41], facilitating nucleation of Cu deposits. Therefore, the spin-formed sample tends to form Cu particles unevenly during the initial stage of film formation. Nevertheless, during the medium and later stages of Cu deposition and foil growth, further thickening of the foil occurs through the reduction of Cu^{2+} on the foil surface. Under this circumstance, the influence of the substrate characteristics on the growth of Cu foil becomes less pronounced, contributing to the Cu foil with similar quality for both the welded joint and spin-formed samples.

5 Conclusions

1) The weld zone is composed of equiaxed α grains with the average grain size of about 16 μm and subgrain α' martensitic phases existing in the α grain interior. The base metal and the spin-formed CP-Ti have equiaxed α grains with the average sizes of about 20 μm for both samples, and no sub-grain features are found.

2) In H_2SO_4 and NaCl solutions, LBW and spin-formed samples possess excellent passivation ability and corrosion resistance. Compared with the spin-formed sample, the welded joint shows slightly lower corrosion resistance in H_2SO_4 solution but better corrosion resistance in NaCl solution. In the strong acidic electroplating solution containing Cl^- , both LBW and spin-formed samples exhibit uniform corrosion morphologies and similar corrosion resistance.

3) At the initial stage of Cu foil growth, the foil formation ability of the welded joint is similar to that of the spin-formed CP-Ti, and the deposited Cu in the weld zone is more uniform and denser. The formed Cu foils have high quality, and the Cu electroplating performances of LBW and spin-formed samples are nearly identical.

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商用纯钛激光焊接接头及旋压成形材料在 $\text{H}_2\text{SO}_4/\text{CuSO}_4$ 电解溶液中的耐腐蚀及铜箔生成行为

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摘要: 采用电化学阻抗谱、动电位极化及浸泡腐蚀等方法对比分析了两组样品的电化学腐蚀形貌及成膜后表面形貌差异, 比较了激光接头样品和旋压成形样品在 $\text{H}_2\text{SO}_4/\text{NaCl}$ 溶液和 CuSO_4 还原电解质中的耐蚀性和成箔能力。结果表明, 在 H_2SO_4 和 NaCl 溶液中, 激光接头样品和旋压成形样品表现出优异的钝化能力和耐腐蚀性。两种样品在含 Cl^- 的强酸性溶液中腐蚀形貌均匀, 耐蚀性相似。同时, 激光接头的铜箔形成能力与旋压成形材料相似, 两种样品上均生成了表面质量较高, 性能差异较小的完整铜箔。

关键词: 钛阴极; 激光焊接; 旋压成形; 腐蚀; 电镀铜箔

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