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Effect of rolling processing on microstructure and electrochemical properties of high active aluminum alloy anode

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Abstract: The effect of rolling processing on the microstructure, electrochemical property and anti-corrosion property of Al-Mg-Sn-Bi-Ga-In alloy anode in alkaline solution (80 ℃, Na_2SnO_3+5 mol/L NaOH) was analyzed by the chronopotentiometry (E-T curves), hydrogen collection tests and modern microstructure analysis. The results show that when the rolling temperature is 370 ℃, the electrochemical activity of Al anode decreases gradually with the increase of pass deformation in rolling, while the anti-corrosion property is improved in the beginning and then declined rapidly. When the pass deformation of rolling is 40%, the Al anode has good electrochemical activity as good as the anti-corrosion property and with the increase of rolling temperature, both electrochemical activity and anti-corrosion property of Al anode increase first and then decrease. When the rolling temperature is 420 ℃, the aluminum alloy anode has the most negative electrode potential of about −1.521 V (vs Hg/HgO) and the lowest hydrogen evolution rate of 0.171 6 mL/(min·cm^2). The optimum comprehensive performance of Al alloy anode is obtained.

Key words: Al alloy anode; microstructure; electrochemical property; anti-corrosion property

1 Introduction

Aluminum alloy has been used as anode material of batteries due to its high capacity and negative potential. However, there are some serious disadvantages such as low electrochemical activity and low anti-corrosion property[1−5]. In recent years, these situations have been greatly improved by both adding specific inhibitors in alkaline electrolyte and optimizing alloying of the Al anode[6−7]. The optimized alloying elements not only destroy the passivity of pellumina and activate the Al anode, but also affect the electrochemical property and microstructure of Al anode[8]. It is indicated that heat treatment has significant effect on the properties of Al anode. For example, the anti-corrosion property of Al anode can be improved by the increase of annealing temperature[9−11]. Uniform annealing can also influence the electrochemical activity of Al anode obviously. If the annealing temperature is below 400 ℃, the electrochemical activity of Al anode decreases with the increase of annealing temperature. When the annealing temperature is higher than 400 ℃, the electrochemical activity becomes better instead[12]. However, the effect of rolling on properties of Al anode has been little investigated. This research mainly focuses on the effect of different rolling processing on the microstructure and properties of a highly active Al alloy anode in order to find an optimum rolling technology.

2 Experimental

2.1 Sample preparation

Conventional melting and casting technique were applied to produce Al-Mg-Sn-Bi-Ga-In alloy anode. The surfaces of the alloy ingots were scraped by machining. The alloy ingots were then heat treated at 510 ℃ for 5 h before quenching in cold water, which was aimed to reduce the crystal defects in alloy and maximize the solid solubility of alloying elements. After that, the ingots were hot-rolled at different pass deformation and rolling temperature to obtain plates with thickness of 0.5 mm.

2.2 Microstructure analysis

Specimens were polished and then submitted to a conventional twin jet electropolishing in 30% HNO_3+

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70% CH_3OH (volume fraction) solution. The microstructure of the Al alloy was observed by a TecnaiG^{2}20 transmission electron microscope (TEM). The surface topography and elements distribution of Al anode were examined by a Sirion-200 scanning electron microscope (SEM) after the surface was burnished, polished, eroded in 0.5%HF solution for 30 s and then washed with distilled water before it was dried. The composition of the segregation phases was analyzed by means of EDAX.

2.3 Performance measurements

Electrochemical measurements were operated in a classical three-electrode glass cell. The working electrode was made of Al alloy chip with 1.0 cm^2 in area. The auxiliary electrode and reference electrode were graphite flake and mercury/mercuric oxide (Hg/HgO) electrode, respectively. The working electrolyte was 5 mol/L NaOH solution with Na_2SnO_3 as inhibitor. The chronopotentiometry with current density of 700 mA/cm^2 was performed at CHI660C/CHI680 electrochemical working station. All the experiments were conducted at a constant temperature of 80 ℃. The hydrogen corrosion rates of the Al anode in alkaline solution (80 ℃, Na_2SnO_3+5 mol/L NaOH) were determined by hydrogen collection method, which is used to estimate the erosion degree of the Al anode under different conditions.

3 Results and discussion

3.1 Effect of pass deformation on microstructure and properties of Al alloy anode

The microstructures of Al alloy anodes with different pass deformations (20%, 30%, 40% and 50%) under 370 ℃ are shown in Fig.1.

When the pass deformation is 20%, the dislocation tangles and cellular structures, as the arrows show in Fig.1(a), are the main structure in Al alloy. With the increase of pass deformation, the microstructure of Al alloy anode transforms from the typical dislocation tangles and cellular structure to subgrain structure and dynamic recrystallized structure. When the pass deformation is 40%, a lot of fine recrystallized grains with clear and straight boundaries, as the arrows show in

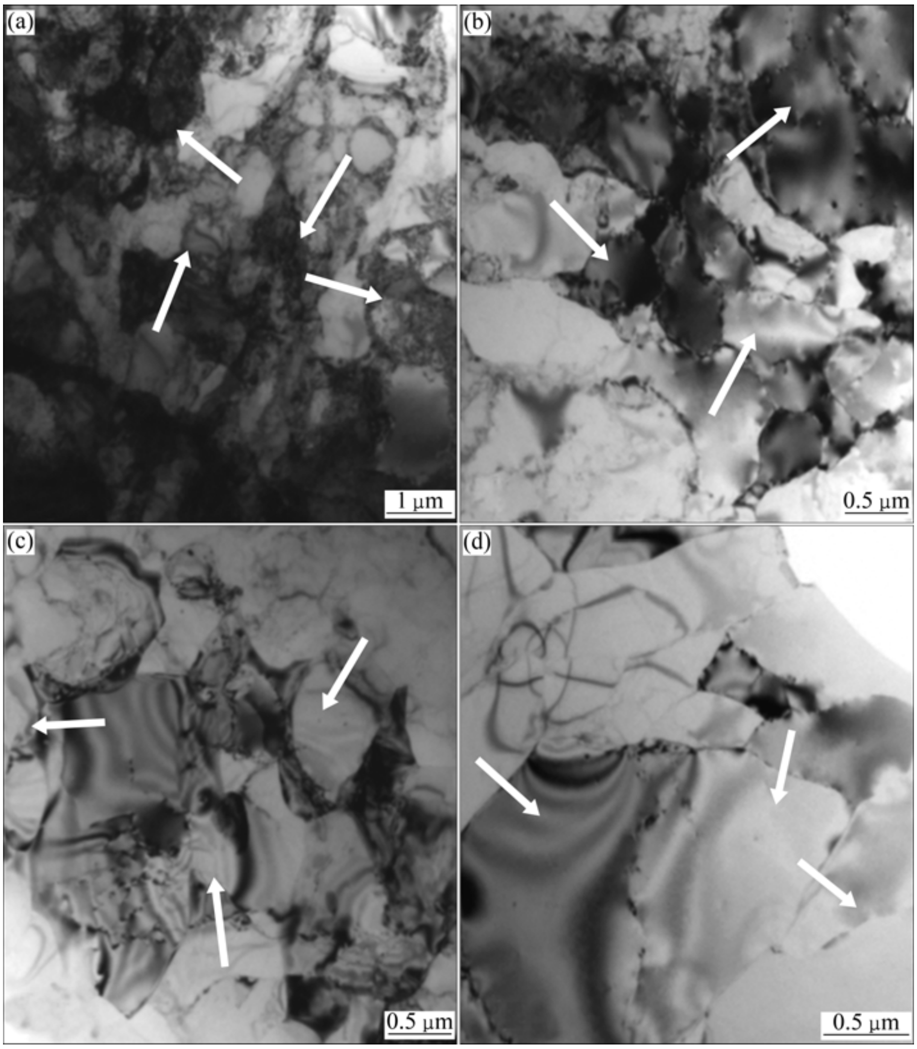

Fig.1 TEM photographs of Al alloy anode under different pass deformations: (a) 20%; (b) 30%; (c) 40%; (d) 50%

Fig.1(c), can be observed in alloys. When the pass deformation is up to 50%, some abnormal big grains are produced due to the second recrystallization, as shown in Fig.1(d).

Fig.2 shows the SEM photographs of the above four samples. It is found that there are lots of fine segregation phases, as shown by the arrows in Fig.2(a), which distribute uniformly in Al alloy anode when the pass deformation is 20%. The quantity of segregation phases decrease with the increase of pass deformation. Particularly, under the pass deformation of 40%, the quantity of segregation phases seems minimum and the corrosion pits become fine and uniform as shown in Fig.2(c). However, when the pass deformation increases to 50%, lots of larger segregation phases, as shown by the arrows in Fig.2(d), are formed in Al anode, and the corrosion degree of Al alloy becomes much more severe.

The EDAX analysis on the segregation phases shown in Fig.3 and Table 1 indicates that the active elements Sn and In are the main components. As active sites, the quantity, size and distribution of segregation phases play an important role in affecting the properties of Al alloy anode[13]. Hence, the pass deformation, which could result in the dynamic recrystallization [14−15], is a key factor for the microstructure controlling of Al anode. A lot of new fine grains, as well as new segregation particles, could be produced by the dynamic recrystallized process in Al alloy, which will reduce the average size of grains and affect the quantity and distribution of segregation phases in Al alloy. The optimum pass deformation is 40% which causes dynamic recrystallization in this study.

The constant-current discharge curves of Al alloy anodes prepared under different pass deformations are shown in Fig.4. It is found that at the rolling temperature of 370 ℃, the higher the pass deformation is, the lower the electrochemical activity of Al anodes is. Particularly, for the pass deformation of 50%, the electrochemical activity of Al anode becomes much lower than that of other anodes, and its discharge curve becomes very unstable. The electrochemical activity of Al anode is mainly controlled by the quantity and distribution of both active points and segregation phases in Al matrix[16]. For the anode prepared at less pass deformation, there are many segregation phases containing active elements Sn and Mn with a much smaller size. Furthermore, segregation phases distribute more uniformly in Al matrix in this case, which leads to the increase of the

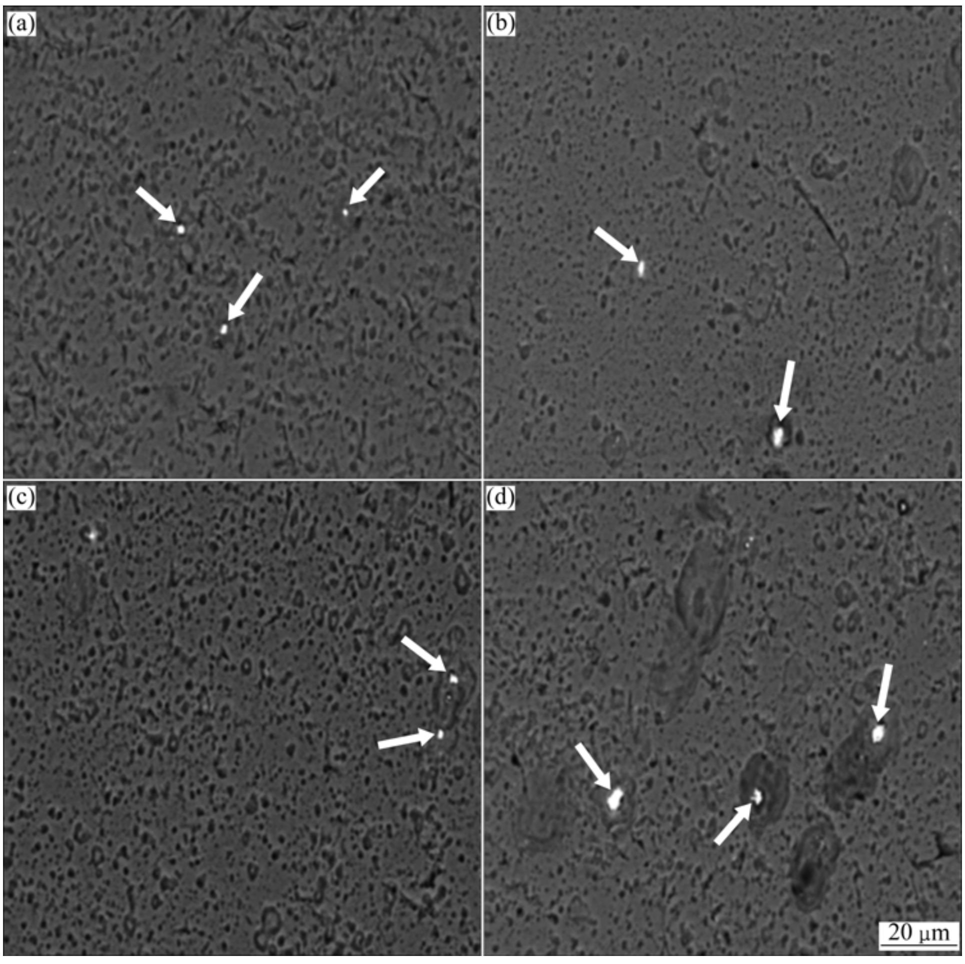

Fig.2 SEM image of Al alloy anode under different pass deformation: (a) 20%; (b) 30%; (c) 40%; (d) 50%

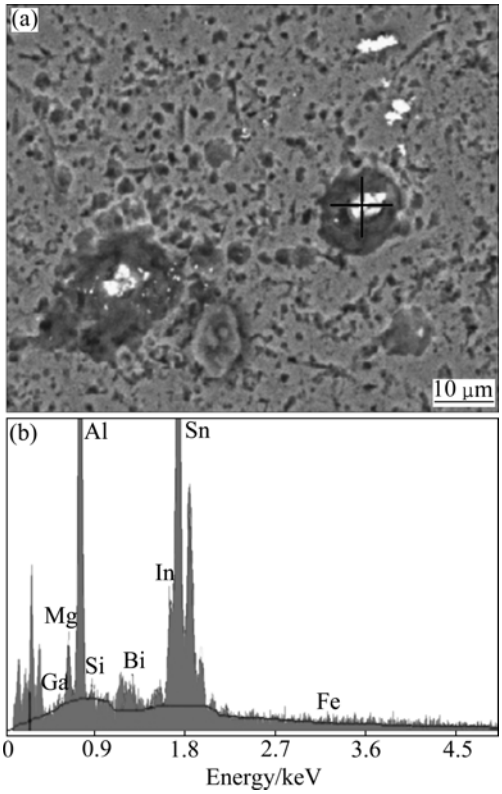

Fig.3 EDAX analysis of segregation phases of Al alloy anode: (a); (b)

Table 1 EDAX results of segregation phases of Al alloy anode

Element	Mass fraction/%	Mole fraction/%
Sn	40.08	15.99
In	11.19	4.62
Bi	3.36	0.76
Ga	0.71	0.48
Fe	1.08	0.92
Si	0.50	0.85
Mg	2.54	5.03
Al	40.55	71.34

active points in Al matrix and improves electrochemical activity of Al anode. With the increase of the pass deformation, the quantity of active points consisting of active elements decreases with increasing the size of segregation phases, and the electrochemical activity of Al anode drops accordingly. When the pass deformation is increased up to 50%, the segregation phases containing active elements are prone to combine together and much larger segregation phases are obtained due to the second recrystallization, which also causes the obvious reduction of solid solubility of active elements and largely impairs the electrochemical activity of Al anode by reducing the quantity of active points.

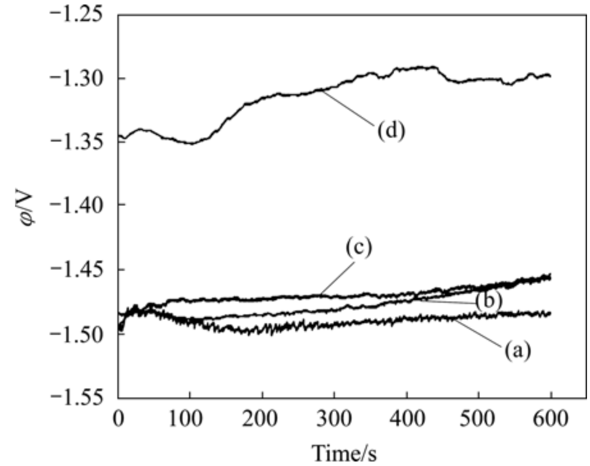

Fig.4 Constant-current discharge curves of Al alloy anode under different pass deformations: (a) 20%; (b) 30%; (c) 40%; (d) 50%

The hydrogen evolution curves and correlative parameters of Al alloy anodes prepared under different pass deformations are shown in Fig.5 and Table 2, respectively. With the increase of pass deformation, the hydrogen corrosion rate decreases until the pass deformation reaches 40% and the Al anode achieves its lowest hydrogen corrosion rate of 0.188 9 mL/(min·cm^2). This means the best anti-corrosion property is obtained. With the pass deformation increases further, the hydrogen corrosion aggravates again. When the pass deformation increases to 50%, the hydrogen corrosion rate reaches to the highest value of 0.237 8 mL/(min·cm^2). The reason of these changes is that before the secondary recrystallization, with the increase of pass deformation, a more uniform microstructure is developed, and the homogeneous distribution of segregation phase is improved. All of these are helpful for the improvement of the anti-corrosion property of Al anode. When the pass deformation increases higher to cause the secondary

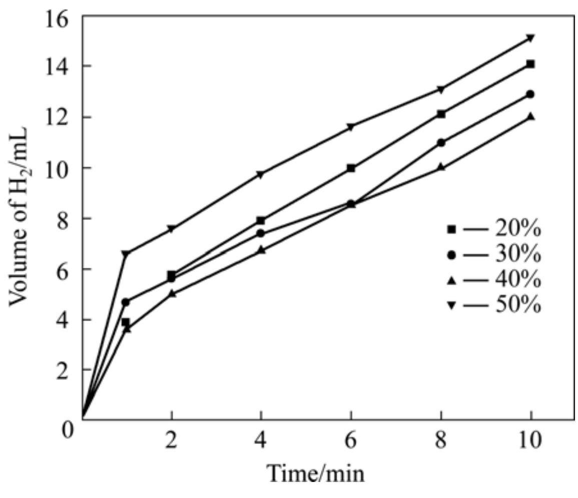

Fig.5 H_2 evolution curves of Al alloy anode under different pass deformations: (a) 20%; (b) 30%; (c) 40%; (d) 50%

Table 2 H_2 evolution test results of Al alloy anode (6.35 cm^2) at 370 ℃ for 10 min under different pass deformations

Pass deformation/ %	Hydrogen evolution volume/ mL	Hydrogen corrosion rate/ ($mL \cdot min^{-1} \cdot cm^{-2}$)
20	14.1	0.222 0
30	12.9	0.203 1
40	12.0	0.188 9
50	15.1	0.237 8

recrystallzation, the new non-uniform microstructure and larger segregation phases are produced, as shown in Fig.2(d). The anti-corrosion property of Al anode deteriorates seriously again due to the abscission of large segregation phases. Therefore, when the pass deformation for the rolling is 40%, the Al anode could achieve good electrochemical activation as well as the anti-corrosion property.

3.2 Effect of rolling temperature on microstructure and properties of Al alloy anode

The TEM photographs of Al alloy anodes under 40% pass deformation at different rolling temperatures are shown in Fig.6. It can be seen that with the increase of rolling temperature, the dislocation tangle and cellular as shown by the arrows in Fig.6(a) decrease significantly, while the sub-grains, as shown by the arrows in Fig.6(b), begin to form, merge and grow. This indicates that the dynamic recrystallization takes place at 370 ℃ rolling. When the rolling temperature increases to 420 ℃, a great deal of sub-structures develop, and some new crystal grains with clear and straight boundaries, as shown by the arrows in Fig.6(c) can be found, which shows that the dynamic recrystallization takes place intensively. When the rolling temperature increases to 470 ℃, some grains merge and much larger recrystallized grains form (as shown by the arrows in Fig.6(d)), which means the secondary dynamic recrystallization takes place.

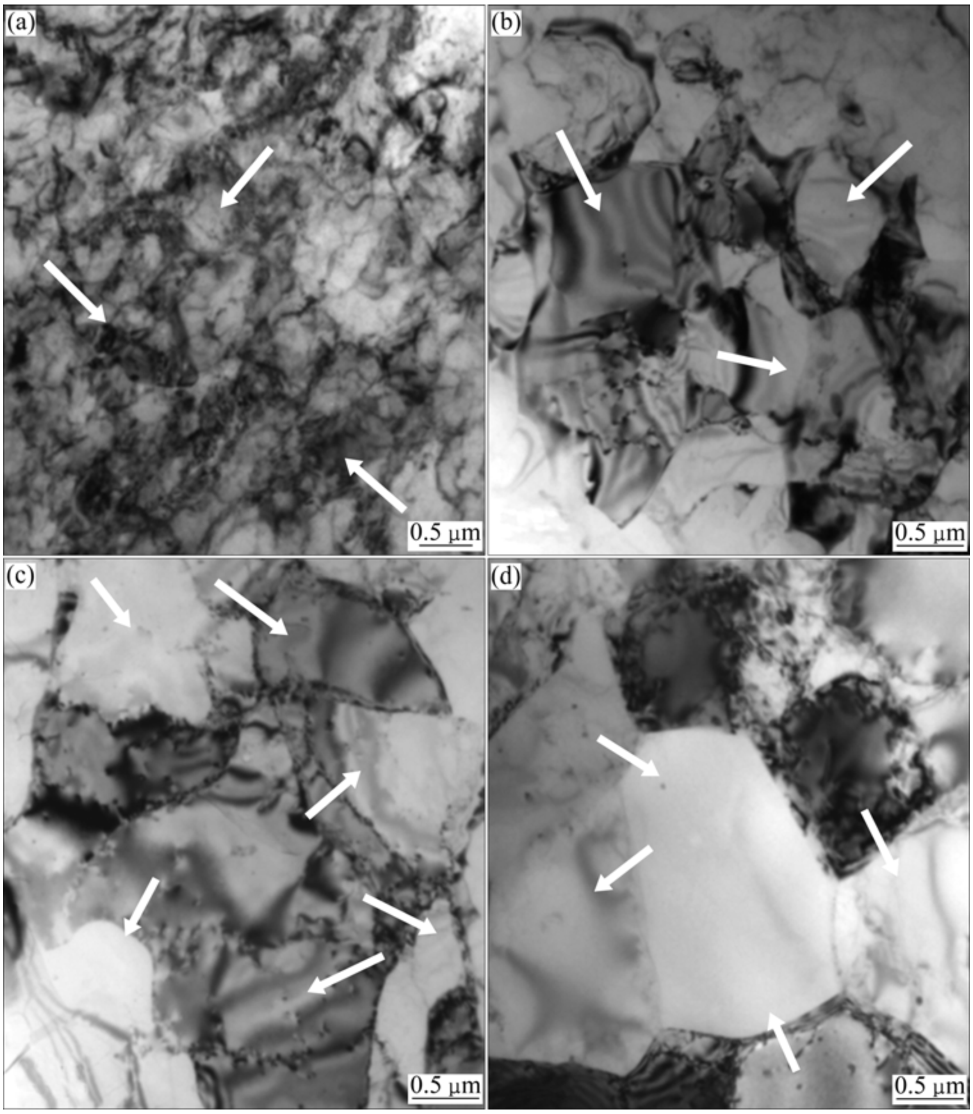

Fig.6 TEM photographs of Al alloy anode under different rolling temperatures: (a) 320 ℃; (b) 370 ℃; (c) 420 ℃; (d) 470 ℃

The SEM images of the above four samples are displayed in Fig.7. For the sample rolled at 320 ℃, a lot of large segregation phases (white area shown in Fig.7(a)), distribute randomly in Al alloy and many deep corrosion pits are formed around them. With the increase of rolling temperature, the microstructure is improved. For the sample rolled at 420 ℃, the segregation phases decrease obviously, their size becomes much smaller than before and the corrosion pits on surface of Al alloy become finer and more uniform. When the rolling temperature increases to 470 ℃, lots of large segregation phases, as shown by the arrows in Fig.7(d), are formed again, and the erosion around the segregation phases is serious.

It can be concluded that the rolling temperature has a great effect on the microstructure of Al anode which is mainly controlled by the dynamic recrystallization and the secondary dynamic recrystallization. A great amount of new fine grains are produced by the dynamic recrystallization, which will reduce the average size of grains. From the dynamic recrystallization, a lot of benefits such as homogeneous distribution of segregation phases, increase of solid solubility of active elements and the decrease of segregation phases could be obtained due to the formation of fine and uniform microstructure. But the second recrystallization has little effect on the improvement of microstructure.

The constant-current discharge curves of Al alloy anodes prepared under different rolling temperatures are shown in Fig.8. It can be seen from the image that the electrode potential of Al anode is closely related to the rolling temperature. At the rolling temperature of 320 ℃, the electrode potential is more positive than others and the electrochemical activity of Al anode is lower correspondingly. With the increase of rolling temperature, the electrode potential of the anode starts to move to the negative direction and the electrochemical activity improves gradually. When the rolling temperature increases to 420 ℃, the Al alloy anode has the most negative electrode potential of about −1.521 V (vs Hg/HgO), which means the best electrochemical activity is obtained. But when the rolling temperature increases to 470 ℃, the electrode potential of the anode moves to the positive direction again, which results in the electro-inferior chemical activity.

All of the variation of the anode discharge curves could be explained by the change of microstructure. When being rolled at low temperature of 320 ℃, Al

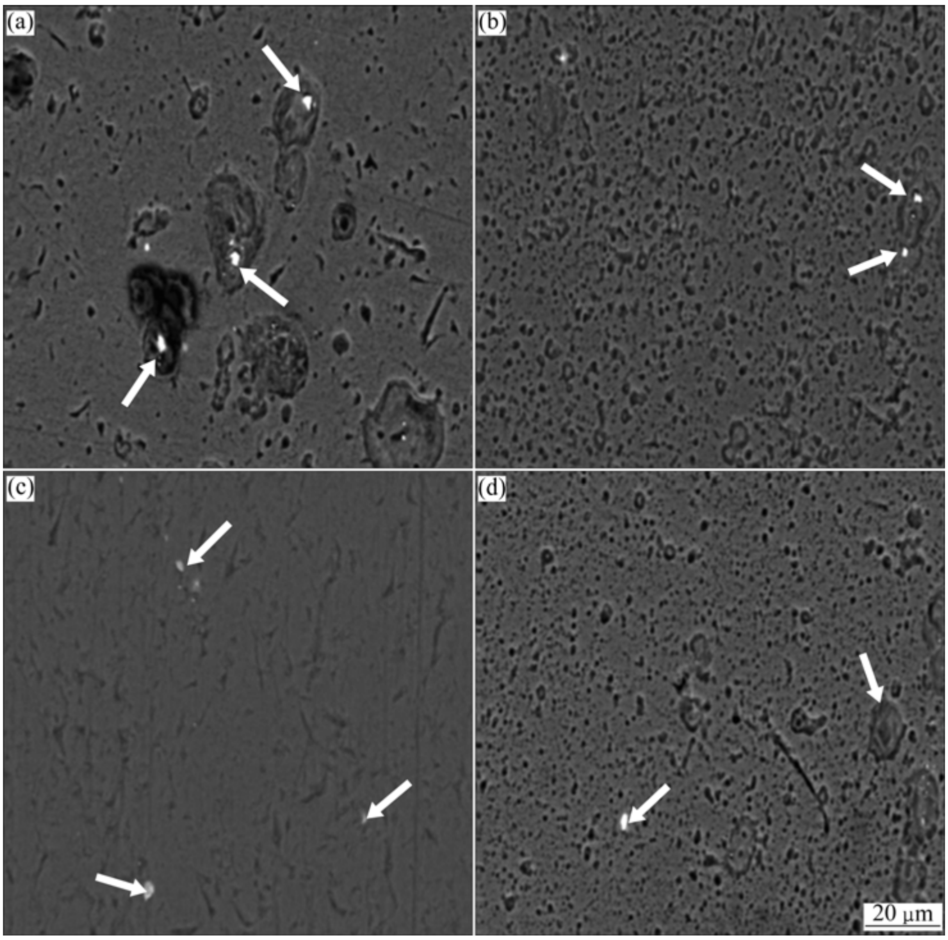

Fig.7 SEM photographs of Al alloy anode under different rolling temperatures: (a) 320 ℃; (b) 370 ℃; (c) 420 ℃; (d) 470 ℃

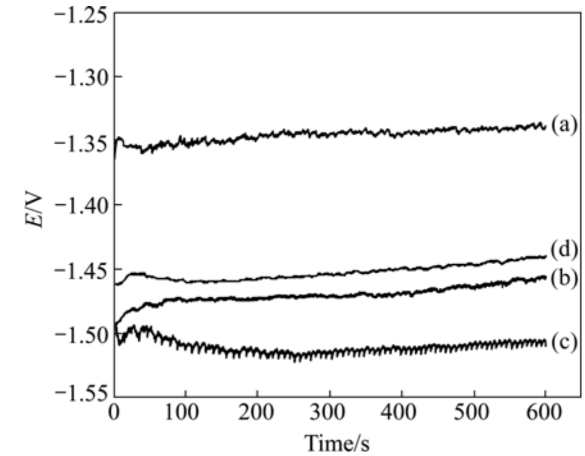

Fig.8 Constant-current discharge curves of Al alloy anode under different rolling temperature: (a) 320 ℃; (b) 370 ℃; (c) 420 ℃; (d) 470 ℃

anode is mainly constructed by disordered dislocation tangles and cellular structure, which makes the alloy in a high energy status. The active elements, like Sn and In, exist in the dislocation tangles and cellular structures because the high energy makes the segregation phase become coarse, which decreases the electrochemical activity of Al anode. The main reason for this is that once the Al anode starts to dissolve, most of the coarse segregations are inclined to strip of the surface of the Al anode (Fig.7(a)). Instead, with the rising of rolling temperature to 370 ℃ or 420 ℃, the active elements are dissolved in Al matrix to a great degree. What is more, the segregation phases and active elements get a homogeneous distribution in Al alloy due to the formation of recrystallization grains by dynamic recrystallization, as shown in Figs.6(b)−(c) and Figs.7(b)−(c). All of these improve the electrochemical activity of Al anode. However, when the rolling temperature increases to 470 ℃ which is higher than the temperature of secondary dynamic recrystallization, a lot of much larger new grains are developed, and the active elements (Sn, In, etc) accumulate in the grain boundaries or their corners, as shown in Fig.6(d) and Fig.7(d), which causes the decrease of the electrochemical activity of anode.

The hydrogen evolution curves of different Al alloy anodes prepared at different rolling temperatures are shown in Fig.9. The results are listed in Table 3.

From Fig.9 and Table 3, it is found that when the rolling temperature is 320 ℃, the hydrogen corrosion is severe because of the high energy status the alloy possesses, and the existence of the larger segregation phases, as shown in Fig.6(a) and Fig.7(a). With the increase of rolling temperature, the hydrogen evolution volume decreases accordingly due to the improvement of microstructure in Al anode. In particular, at 420 ℃, the hydrogen corrosion rate of Al anode reaches the lowest value of 0.171 6 mL/(min·cm^2). This indicates that Al anode achieves the optimum anti-corrosion property at this rolling temperature. When the rolling temperature rises further to 470 ℃, the hydrogen evolution volume rises obviously again due to the change of microstructure mentioned above.

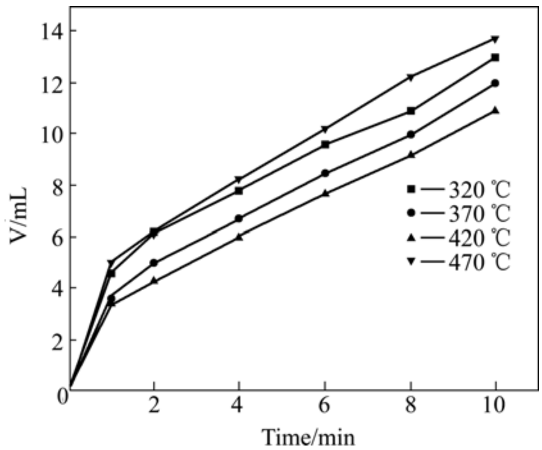

Fig.9 H_2 evolution curves of Al alloy anode at different rolling temperature: (a) 320 ℃; (b) 370 ℃; (c) 420 ℃; (d) 470 ℃

Table 3 H_2 evolution test results of Al alloy anode (6.35 cm^2) with pass deformation of 40% at different rolling temperatures for 10 min

Rolling temperature/ ℃	Hydrogen evolution volume/ mL	Hydrogen corrosion rate/ (mL·min^{-1}·cm^{-2})
320	13.1	0.204 7
370	12.0	0.188 9
420	10.9	0.171 6
470	13.7	0.215 7

4 Conclusions

1) The pass deformation and rolling temperature have great effects on the microstructures, electrochemical activity and anti-corrosion property of Al anode. With the increase of pass deformation and rolling temperature, the microstructure of the Al alloy anode undergoes a transformation from the typical dislocation tangles and cellular structure to the dynamic recrystallized structure, and finally to the secondary dynamically recrystallized structure. The optimum microstructure could be achieved by the dynamically recrystallization.

2) The optimum parameters for the pass deformation and the rolling temperature are 40% and 420 ℃, respectively. In the Al alloy anode prepared under the optimum condition, the active elements, Sn, In, etc,

distribute uniformly and only small amount of segregation phases exist. The optimum aluminum alloy anode has the most negative electrode potential with the value of about −1.521 V (vs Hg/HgO) and the lowest hydrogen evolution rate of 0.171 6 mL/(min·cm^2).

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