Effect of nano-segregation phases on electrochemical property of high active Al alloy anode

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Abstract. The effect of nano-segregation phases formed during rolling process on the electrochemical property of Al-Mg-Sn-Bi-Ga-In alloy anode in alkaline solution (80°C, Na₂SnO₃ + 5mol/L NaOH) was analyzed according to the chronopotentiometry (E-T curves), hydrogen collection tests and modern microstructure analysis. The results show that when controlling the rolling temperature and pass deformation at 370°C and 40% respectively, the Al alloy anode undergoes the dynamic recrystallization, which benefits to the uniform distribution of nano-segregation phases and improvement of electrochemical property of Al alloy anode. The optimum Al alloy anode has the more negative electrode potential of about -1.48V (vs.Hg/HgO) and the lower hydrogen evolution rate of 0.1889mL/(min·cm²).

Key words. Al alloy anode; nano-segregation phases; electrochemical property; rolling process

1. Introduction
The aluminum / air (Al/O₂) fuel cells or aluminum / silver oxide (Al/AgO) sea-water cells, with alkaline sea-water as electrolyte, oxygen in the air or silver oxide as cathode, and the aluminum alloy with high electrochemical equivalent and negative electrode potential as anode, have hold the leading position among the cells with excellent performance due to their high specific energy, high specific capacity, free contamination and no noise [1-3]. In addition, the other advantages of aluminum alloy, such as rich in storage, easy to manufacture and so on, will result in the low cost of this kind of cells [4]. Since 1970s, the research on active aluminum alloy anode has been paid great attention by the energy, transportation, telecom and defense departments in many countries [5-7]. However, during the working process, pure aluminum reacts intensively with electrolyte and produces a large amount of hydrogen because of the solution of oxide film on aluminum surface. Especially, when the cell works under large current density, the stable working potential will become fairly low and the anode...
polarization is very serious. In recent years, these situations had been greatly improved by optimizing alloying of the Al anode [8]. It has been indicated that different heat treatment techniques have significant effect on microstructure and properties of Al anode [9-11], which will be mainly attributed to the size, shape and distribution of segregation phases formed during heat treating. Especially when the size of segregation phase reduces into the nanometer range, the Al anode exhibits interesting electrochemical property compared to other anode materials. However, the effect of nano-segregation phases formed during rolling process on electrochemical properties of Al anode has been little investigated. This research mainly focuses on investigating the effect of nano-segregation phases on the microstructure and properties of a high active Al alloy anode. The main purpose is to find an optimum rolling technology.

2. Experimental procedure

2.1. Sample preparation

Conventional melting and casting technique had been 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 for 5 h at 510°C before quenching them with 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 0.5mm thickness.

2.2. Microstructure analysis

The microstructure of the Al alloy was studied by a TecnaiG20 TEM after being polished by machine and then submitted to a conventional twin jet electropolishing in 30%HNO3 + 70%CH3OH (vt%) solution. The surface topography and alloy elements distribution of Al anode were examined by Sirion-200 SEM after the surface was burnished and 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 also 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 1.0cm² in area. The auxiliary electrode and reference electrode was graphite flake and mercury/mercuric oxide (Hg/HgO) electrode respectively. The working electrolyte was 5mol/L NaOH solution with Na2SnO3 as inhibitor. The chronopotentiometry with current density of 700mA/cm² was performed at CHI660C/CHI680 electrochemical working station. All the experiments were conducted at a constant temperature of 80°C. The hydrogen corrosion rates of the Al anode in alkaline solution (80°C, Na2SnO3 + 5mol/L NaOH) were determined by hydrogen collection method, which could be used to estimate the erosion degree of the Al anode under different conditions.

3. Results and discussions

3.1. Effect of pass deformation on the nano-segregation phases

The TEM photographs of Al alloy anode with different pass deformation under 370°C are shown in figure 1.
Figure 1. TEM photographs of Al alloy anode under different pass deformation: (a) 20\%, (b) 30\%, (c) 40\% and (d) 50\%.

With the increase of pass deformation, the microstructure of Al alloy anode undergoes a transformation from the typical dislocation tangle and cellular structure to the dynamic recrystallized structure, finally to the secondary dynamic recrystallized structure. When the pass deformation is 20\%, the dislocation tangles and cellular structures, as the arrows show in figure 1 (a), are the main structure in Al alloy. When the pass deformation is 40\%, a lot of fine recrystallized grains with clear and straight boundary, as the white arrows show in figure 1 (c), can be observed in alloys. At the same time, lots of nano-segregation phases with the size of 100-200nm, as the black arrows show, can also be found among the grain boundary. When the pass deformation is up to 50\%, some abnormal big grains have been produced due to the second recrystallization, which promotes the gather of nano-segregation phases, as the black arrows show in figure 1 (d).

Figure 2. SEM photographs of Al alloy anode under different pass deformation: (a) 40\% and (b) 50\%.

Figure 2 is the SEM photographs of above samples under different pass deformation. It can be found that there are lots of nano-segregation phases, as the arrows show in figure 2 (a), which distributes uniformly due to the dynamic recrystallized under pass deformation of 40\%. And the corrosion pits on Al surface also seem to be finer and uniform. While under the pass deformation of 50\%, lots of large size segregation phases, as the arrows show in figure 2 (b), begin to form due to the gather of nano-segregation phases. The corrosion degree of Al alloy becomes much more severe correspondingly. The EDAX microanalysis on the nano-segregation phases according to figure 3 and
Table 1 shows that the active elements Sn, In are the main components, which demonstrates that the main body of the nano-segregation phases is Sn-rich phase. As active sites, the distribution of nano-segregation phases plays an important role in improving the properties of Al alloy anode.

**Figure 3.** EDAX analysis of nano-segregation phases of Al alloy anode.

![EDAX analysis](image)

**Table 1.** Quantity results of nano-segregation phases of Al alloy anode.

| element | Sn   | In   | Bi  | Ga  | Fe  | Si  | Mg  | Al  |
|---------|------|------|-----|-----|-----|-----|-----|-----|
| mass fraction, % | 40.08 | 11.19 | 3.36 | 0.71 | 1.08 | 0.50 | 2.54 | 40.55 |
| mole fraction, % | 15.99 | 4.62 | 0.76 | 0.48 | 0.92 | 0.85 | 5.03 | 71.34 |

Hence, the pass deformation, which could result in dynamic recrystallization [12,13], is a key factor for the formation and uniform distribution of nano-segregation phases in Al anode. A lot of new fine grains could be produced by the dynamic recrystallized process, which will reduce the average size of grains and affect the precipitation and distribution of nano-segregation phases in Al alloy. The optimum pass deformation which causes dynamic recrystallization is 40% in our study.

### 3.2. Effect of nano-segregation phases on the properties of Al anode

Figure 4 is the constant-current discharge curves and hydrogen evolution curves of Al alloy anodes prepared under different pass deformations in 80°C, Na₂SnO₃ + 5mol/L NaOH electrolyte with current density of 700mA/cm². The correlative parameters are listed in table 2. It can be found from figure 4(a) that under the pass deformation of 40% which benefits to the uniform distribution of nano-segregation phases, the Al alloy anodes own the more negative electrode potential of about -1.48V (vs.Hg/HgO). But when the pass deformation increases to 50%, the electrochemical activity of Al anode becomes much lower than other anodes, and its discharge curve also becomes much unstable. The electrochemical activity of Al anode is mainly controlled by the distribution of nano-segregation phases in Al matrix. For the anodes prepared at the pass deformation of 40%, the nano-segregation phases containing active elements Sn, In, is of the much smaller size, and distribute homogeneously in Al matrix, which leads to the increase of the quantity of active points in Al matrix and improves electrochemical activity of Al anode. With the increase of the pass deformation, the quantity of active point decreases with the gather of nano-segregation phase, the electrochemical activity of Al anode...
drops accordingly.

![Graph](image)

**Figure 4.** Constant-current discharge curves (a) and hydrogen evolution curves (b) of Al anode under different pass deformation: (1) 40% and (2) 50%.

**Table 2.** H₂ evolution parameters of Al alloy anode (6.35cm²) under different pass deformation.

| Rolling Temperature/(℃) | Pass deformation/% | Working time/min | Hydrogen volume/mL | Corrosion rate/mL·min⁻¹·cm⁻² |
|-------------------------|-------------------|----------------|-------------------|-----------------------------|
| 370                     | 20                |                | 14.1              | 0.2220                       |
|                         | 30                | 10             | 12.9              | 0.2031                       |
|                         | 40                |                | 12.0              | 0.1889                       |
|                         | 50                |                | 15.1              | 0.2378                       |

From figure 4 (b) and table 2, it could be found that the Al anode achieves its lowest hydrogen corrosion rate of 0.1889mL/cm²·min due to the uniform distribution of nano-segregation phases under pass deformation of 40%. That means, the best anti-corrosion property has been obtained. While the corrosion degree for other samples are still severe. The reason of these changes is that under pass deformation of 40%, the uniform distribution of nano-segregation phases is improved, and a more homogeneous microstructure is developed. All of these are helpful for the improvement of the anti-corrosion property of Al anode.

**4. Conclusions**

The pass deformation had great effects on the formation and distribution of nano-segregation phases in Al anode. With the increase of pass deformation, the microstructure of the Al alloy anode underwent a transformation from the typical dislocation tangle and cellular structure to the dynamic recrystallized structure, finally to the secondary dynamic recrystallized structure. The optimum size and distribution of nano-segregation phases could be achieved by the dynamic recrystallization under pass deformation of 40%. The uniform distribution of nano-segregation phases promoted the Al alloy anode to achieve well electrochemical activation as well as the anti-corrosion property. The optimum aluminum alloy anode had the more negative electrode potential with the value of about -1.48V (vs.Hg/HgO) and the lower hydrogen evolution rate of 0.1889mL/ (min·cm²).
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