

Effect of microstructure on specific capacitance of AA3003 aluminum alloy foils^①

ZHANG Xir-ming(张新明), JIN Li(靳 丽), XIAO Ya-qing(肖亚庆), JIAN Xiong(蹇 雄)
(College of Materials Science and Engineering, Central South University, Changsha 410083, China)

Abstract: By means of OM, EDS, SEM and TEM, the effect of microstructures of AA3003 aluminum alloy foils on specific capacitance was investigated. The results show that the specific capacitance of the cathode aluminum foils depends on the microstructures of the foils, including intermetallic compound (Mn, Fe)Al₆ and Al matrix, tangled dislocations in the regions adjacent to the intermetallic particles, and smaller and dispersed particles. Because the dislocation interaction with larger particles gives rise to high local lattice curvature in the matrix, which can be preferentially dissolved when etched, which results in serious remnant metal powders on the foil surface. Solid solution at 630 °C, quenching in water and aging at 60 °C may increase the number of the second phase particles, and reduce the large particles, so that the capacitance of the cathode foils becomes higher and almost no powders remain on the surface of the foil. By means of aging after quenching, the precipitated particles and etch-pit density in the foil increase obviously, therefore the favourable microstructures can be produced to improve the specific capacitance of the foils.

Key words: AA3003 aluminum alloy; cathode foil; microstructure; specific capacitance

CLC number: TG 335.5

Document code: A

1 INTRODUCTION

In recent years, high specific capacitance has come to be pursued for small electrolytic capacitors. The microstructures of the aluminum foil will influence the specific capacitance of the capacitors seriously. AA3003 aluminium alloy is often used for the cathode of the capacitors^[1-7], containing Mn, Cu, Mg, Si and Fe, and showing an excellent corrosion resistance. The solubility of Mn in Al matrix is very low at room temperature, and Mn is often precipitated in the form of MnAl₆. The soluble iron in Al matrix is very limited, often precipitated in the form of (Mn, Fe)Al₆. If dispersed (Mn, Fe)Al₆ is homogeneously precipitated in the matrix, so that the etched surface of the foil can considerably increase in area for the capacitors^[4]. However, when Mn content exceeds 1.5%, loss in etching and recession may increase considerably^[7]. And the corrosion character of the cathode foil is also affected by hot rolling, annealing treatment and cold rolling^[5], in which the annealing temperature, the cooling rate and the reduction ratio are always important factors^[5, 6]. The cathode aluminum foil needs to be subjected to chemical etching to increase surface area, however, the remnant metal powders are often left, which results in commercial uselessness when it is severe.

For higher capacitance, selecting a suitable heat-

treatment process which leads to uniform dispersion of intermetallic compounds is very important to AA3003 aluminium alloy.

In this study, the effect of heat-treatment on the microstructures, consequently, on the specific capacitance of the cathode aluminum foils is investigated.

2 EXPERIMENTAL

The chemical compositions of DC ingot of the studied AA3003 aluminum alloy is given in Table 1. The ingot was homogenized, hot-rolled, cold-rolled, intermediate annealed and cold-rolled down to 0.5 mm in thickness, then heat-treated by different processes and at last cold-rolled down to 0.05 mm. The identification symbols of the prepared sheets and foils are shown in Fig. 1. The foils were etched in 1.0 mol/L HCl and AlCl₃ (200 g/L) at 100 °C for 12 s, then washed by HNO₃, H₃PO₄ and distilled water, and finally dried.

The microstructures were examined by KYKY2800 SEM, and H800 TEM, the photographs of the dislocation etch-pits were obtained by

Table 1 Chemical compositions of

AA3003 aluminum alloy (mass fraction, %)

Cu	Mg	Mn	Fe	Si	Al
0.2	0.04	1.24	0.56	0.60	Balance

① **Foundation item:** Project(G1999004908) supported by the National Key Fundamental Research and Development Program of China

Received date: 2002 - 09 - 04; **Accepted date:** 2002 - 11 - 18

Correspondence: ZHANG Xir-ming, Professor; Tel: + 86-731-8830265; E-mail: xmzhang@mail.csu.edu.cn

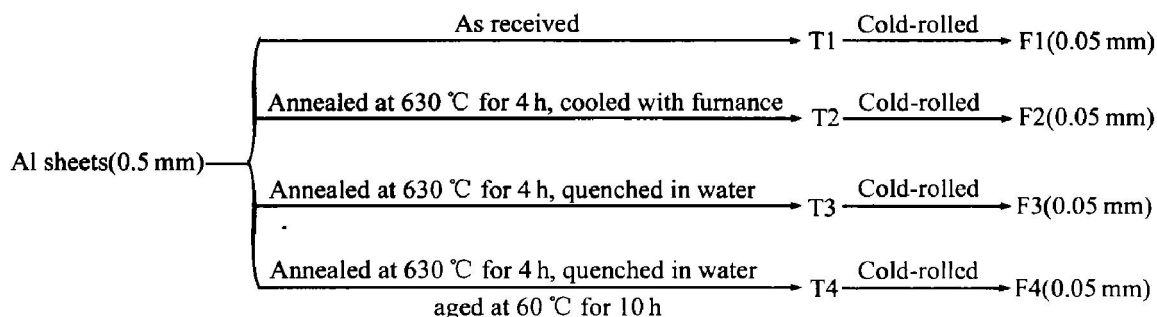


Fig. 1 Scheme of preparation process of studied samples

POLYVAR-MET optical microscopy, and the compositions of second phases were determined by X-ray energy dispersed spectroscopy (EDS), the specific capacitances were determined by the capacitance measuring instrument TH2615E.

3 RESULTS

The foils are etched and the results of the capacitance test are listed in Table 2, and the mass loss of the foil treated by different processes after etching is shown in Fig. 2. As shown in Table 2, the specific capacitance of the foils F1, F2 and F3 decreases according to the order: $C(F1) > C(F3) > C(F2)$, and the specific capacitance $C(F4)$ of the foil F4 is the highest. The mass loss shown in Fig. 2 decreases according to the order: F1, F2 and F3, then increases to F4. The surface character in Table 2 indicates that the black surfaces of the etched foils F1 and F2 are covered by more black powder particles, and that there are no remnant powders to be seen on the surfaces of the foils F3 and F4.

Table 2 Surface corrosion character and specific capacitance of cathode foils

No.	Etching time/s	Surface corrosion character	Specific capacitance/ ($\mu\text{F}\cdot\text{cm}^{-2}$)
F1	12	Black	510
F2	12	Black	375
F3	12	Bright	450
F4	12	Bright	600

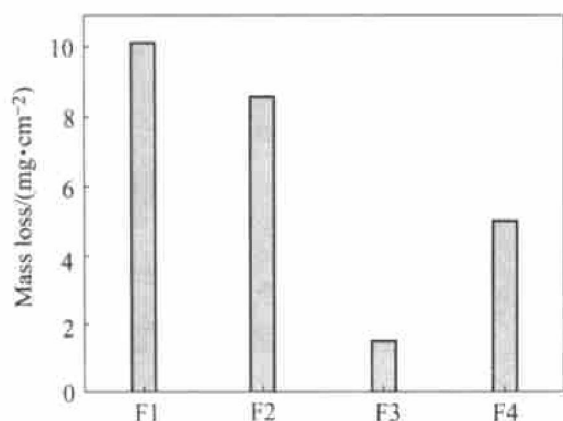


Fig. 2 Etched mass loss of foils treated by different processes

4 DISCUSSION

4.1 Effect of heat treatment on microstructures of AA3003 aluminium sheets

The amount of the alloy elements in the aluminum matrix depends upon their solid solubility and their diffusion rate^[8]. The microstructures of AA3003 aluminium alloy consisted of intermetallic compound MnAl_6 or $(\text{Mn}, \text{Fe})\text{Al}_6$ and Al matrix, and the sizes of the intermetallic particles are important to capacitance because they affect the distribution of dislocation in the aluminum foil after plastic deformation. The microstructures shown in Fig. 3(a) indicate that the intermetallic particles have non-uniform sizes, and some particles ($5-6\ \mu\text{m}$) are much larger than the others ($2-3\ \mu\text{m}$). The result from EDS for spot A in Fig. 3(a), listed in Table 3, suggests that the second phases must be $(\text{Mn}, \text{Fe})\text{Al}_6$, which decrease (Fig. 3(b)) in the aluminum sheet T2 compared to the sheet T1 (Fig. 3(a)). According to $\text{Al}-\text{Mn}$ phase diagram, the second phase particles of MnAl_6 or $(\text{Mn}, \text{Fe})\text{Al}_6$ would be dissolved at $630\ ^\circ\text{C}$ for $4\ \text{h}$ ^[8]. The thermal exposure in the cooling furnace makes the deposition of Mn from supersaturated matrix onto the pre-existing intermetallics^[9] and coarsens the $(\text{Mn}, \text{Fe})\text{Al}_6$ structure (Fig. 3(b)), so that the particle size reaches $8-9\ \mu\text{m}$. The microstructures of the aluminum sheet T3, as shown in Fig. 3(c), indicate that the second phase particles ($1-2\ \mu\text{m}$) are more and smaller than those in Fig. 3(b). Some particles including the larger are dissolved when heated at $630\ ^\circ\text{C}$. A lot of new particles will be precipitated when the sheets are aged after quenching in water because the higher undercooling is favourable to a higher nucleation rate. The microstructures of the sheet T4 aged at $60\ ^\circ\text{C}$, as shown in Fig. 3(d), indicate that the number of the second phase particles with uniform size increases markedly compared to that in Fig. 3(c).

Table 3 EDS result for spot A in Fig. 3(a)
(mass fraction, %)

Al	Fe	Mn	Si
80.29	9.64	10.08	—

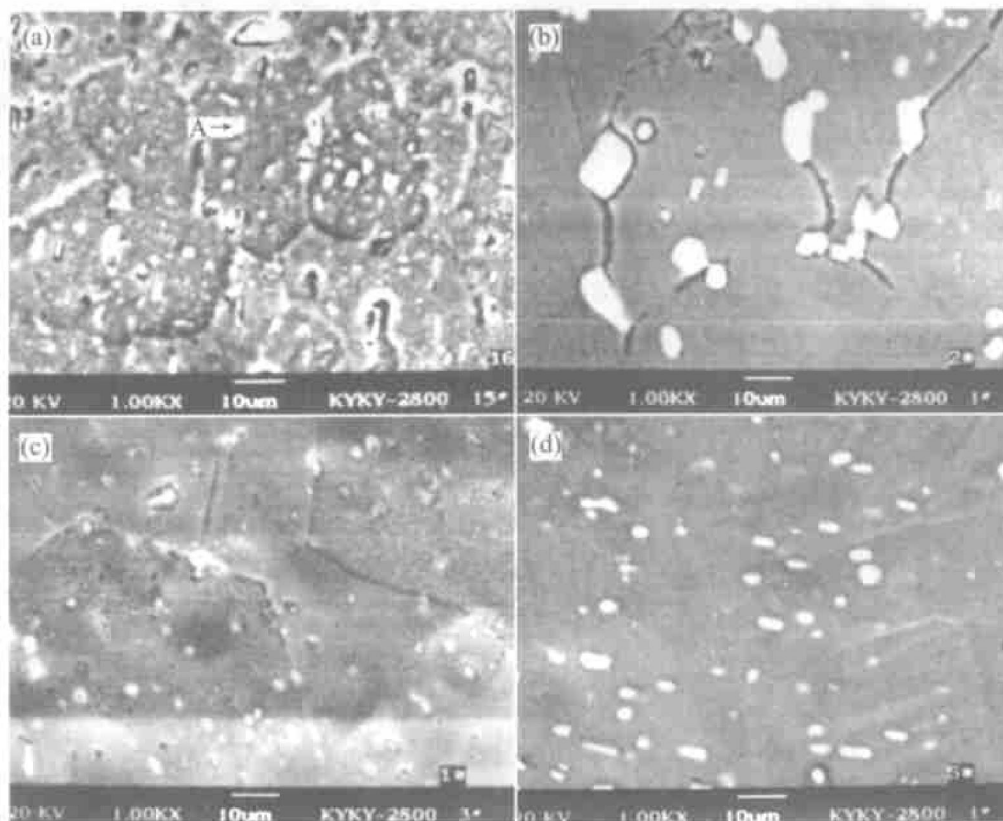


Fig. 3 SEM photographs of sheets (0.5 mm)

(a) -T1; (b) -T2; (c) -T3; (d) -T4

4.2 Effect of microstructures on capacitance of foils

The microstructures will affect the etching, consequently, the specific capacitance. The etching morphology of the foil F1 in the mixed solution of 1.0 mol/L HCl and AlCl_3 (200 g/L) for 2 s, as shown in Fig. 4, indicates that the preferentially etched pits in the regions are adjacent to the larger intermetallic particles. As shown in Fig. 5(a), the dislocations are tangled in the regions adjacent to larger particles, near which the matrix is preferentially dissolved in the etching solution due to the tangled dislocations and high local lattice curvature^[10]. Fig. 5(b) shows that the second phases lead to a much higher dislocation density and produce homogeneous distribution of dislocations.

Zhang et al^[11] suggested that pitting might be

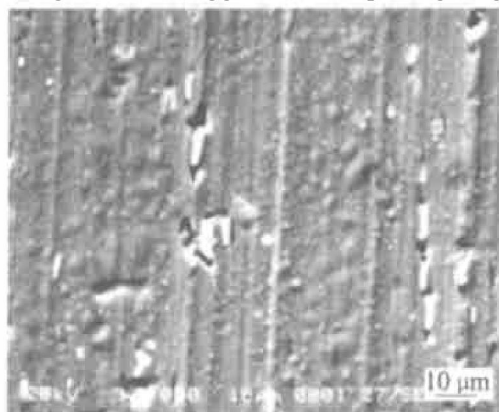


Fig. 4 Corrosion surface of foil F1 etched for 2 s

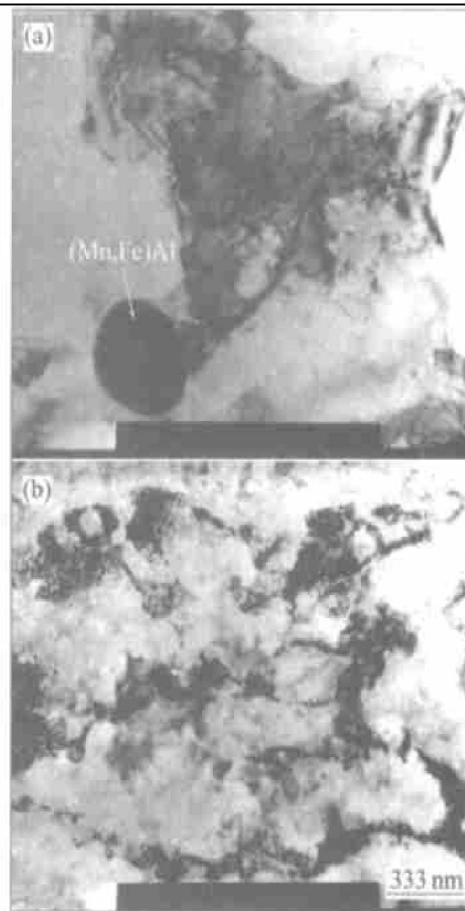


Fig. 5 TEM photographs of foils F1 and F3

(a) —Dislocation tangled near particles in foil F1;
(b) —Distribution of dislocations in foil F3

the result of dissolving of the metal at flaws and defects within the surface oxide when the bare metal was exposed to the aggressive anion in the electrolyte, and that the formation of flaws was a necessary condition for pit initiation. The surface of the aluminum foil with more particles was more susceptible to etching^[12], so that the etch-pit density was higher there. The dislocation etch pits of the foils are shown in Fig. 6, and it indicates that etch-pits decrease (Figs. 6(a) and (b)) from F1 to F2 with the number decreasing of the particles, and that in the foil F3 (Fig. 6(c)) is less than in the foil F1 (Fig. 6 (a)), but more than in the foil F2 (Fig. 6(b)), and that in the foil F4 is the highest (Fig. 6 (d)).

There are fewer particles in the sheet T2, and their sizes are larger, so that the specific capacitance of the foil F2 is lower and serious remnant powders cover in the surface of the foil. Fewer particles are seen in the sheet T3 and the smaller particles may lead to the lower specific capacitance and lower mass loss of the foil F3. However, in the sheet T4, much smaller particles are precipitated (Fig. 3 (d)), and there are no powders to be seen on the surface of the foil F4 after etching. All the results suggest that the sizes and distribution of the second phase particles can affect the specific capacitance and the surface morphology of the etched foils. The more the smaller par-

ticles, the higher the specific capacitance, and the less the powders on the etched foil surface. Therefore, for higher capacitance and no remnant powders on the surface of the foil, it is suggested that the process of solid solution at 630 °C, quenching in water and aging at 60 °C can be practicable to the AA3003 aluminium alloy foils.

5 CONCLUSION

The specific capacitance of the AA3003 aluminum alloy foil depends on the microstructures including sizes, dispersed distribution of intermetallic compound (Mn, Fe)Al₆, and the dislocations tangled in the regions adjacent to the intermetallic particles. The smaller and dispersed particles can lead to a homogeneous distribution of dislocations and etch pits, consequently, to a high specific capacitance of the aluminum foil. The dislocations interaction with larger particles will give rise to high local lattice curvature, so that the matrix can be preferentially dissolved when etched. Solid solution at 630 °C, quenching in water and aging at 60 °C can increase the number of the dispersed fine particles and reduce the large particles, so that the specific capacitance of the foil becomes much higher.

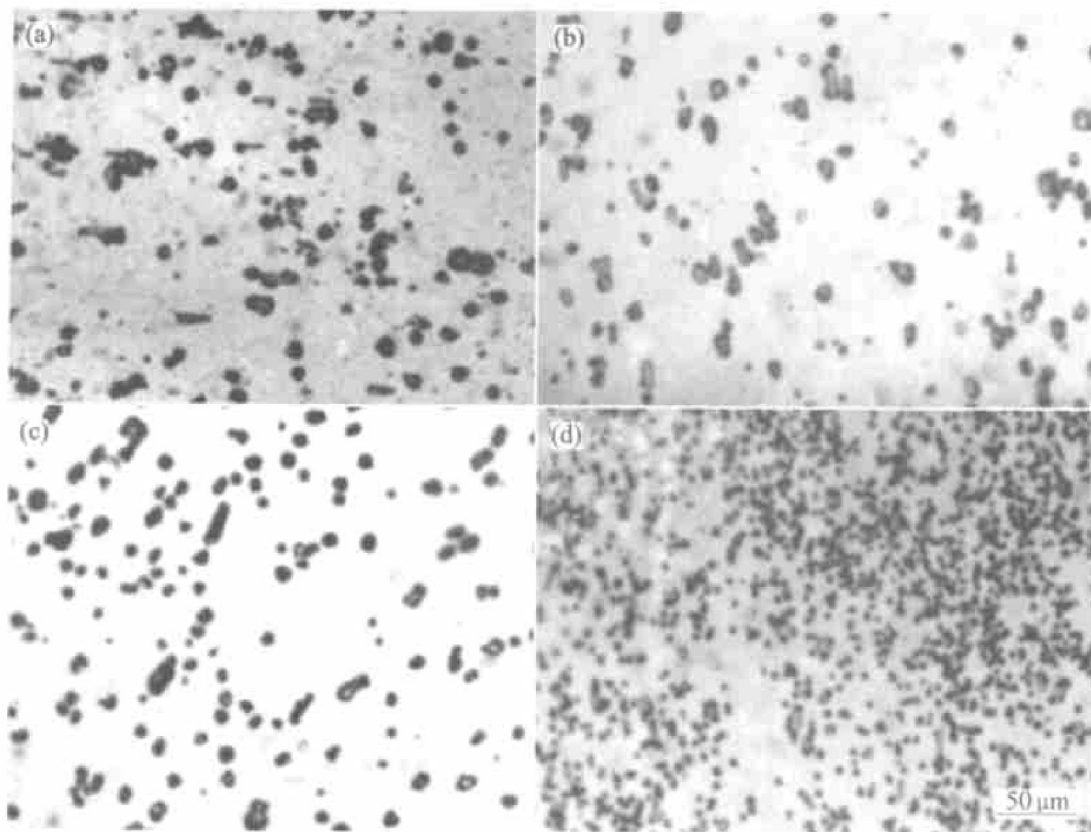


Fig. 6 Morphologies of etch-pits of foils
(a) —F1; (b) —F2; (c) —F3; (d) —F4

REFERENCES

- [1] Aluminium S. Aluminum Alloy Foil for Cathode of Electrolytic Capacitor[P]. JP88106A-KoKai(00088106/JP-A-KoKai), Japan, 1988-01-05.
- [2] Aluminium S. Aluminum Alloy Foil for Cathode of Electrolytic Capacitor [P]. JP88153811A-KoKai(88153811/JP-A-KoKai), Japan, 1988-06-27.
- [3] Mitsubishi Aluminium Co. Ltd. Aluminum Alloy Containing Manganese, Iron and Copper for Use as Cathode in Electrolytic Capacitor[P]. JP51097519, Japan, 1975-02-26.
- [4] Mitsubishi Light Metal Industries. Aluminum Alloy Foil Cathode for Electrolytic Capacitor[P]. JAJ81127759-KoKai(81127759/JA-J-KoKai), Japan, 1980-03-07.
- [5] Sumitomo Light Metals. Manufacturing Aluminum Foil for Electrolytic Capacitor Cathode[P]. JP88137505A-KoKai(88137505/JP-A-KoKai), Japan, 1988-06-09.
- [6] Sumitomo Light Metals. Aluminum Foil Used as Electrolytic Capacitor Cathode[P]. JP88137504A-KoKai(88137504/JP-A-KoKai), Japan, 1988-06-09.
- [7] Aluminium S. Aluminum Alloy Foil for Electrolytic Capacitor Cathode[P]. JAJ54135347(54135347/JA-J), Japan, 1978-04-13.
- [8] Kattamis TZ, Storrs, Merchant HD, et al. Homogenization and coarsening in cast 3004 aluminium alloy [J]. Aluminium, 1989, 65(4): 367-376.
- [9] Scully J R, Peebles D E, Romig A D, et al. Metallurgical factors influencing the corrosion of aluminum, Al-Cu, and Al-Si alloy thin films in dilute hydrofluoric solution [J]. Metallurgical Transaction A, 1992, 23A: 2641-2655.
- [10] Martin J W, Doherty R D. Stability of Microstructure in Metallic Systems, Cambridge Solid State Science Series [M]. Cambridge: Cambridge University Press, 1976. 96-101.
- [11] Zhang X, Lo Russo S, Zandolin S, et al. The pitting behavior of Al3103 implanted with molybdenum [J]. Corrosion Science, 2001, 43(11): 85-97.
- [12] Lunder O, Nisancioglu K. The effect of alkaline etch Pretreatment on the pitting corrosion of wrought aluminum[J]. Corrosion, 1988, 44(7): 414-422.

(Edited by HE Xue-feng)