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EFFECT OF HOMOGENIZATION TREATMENT CONDITIONS ON THE RECRYSTALLIZATION BEHAVIOR OF AL-1.2MN ALUMINUM ALLOY SHEETS

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Abstract

Aluminum foil is commonly used as a cathode current collector within lithium ion battery. To reduce thickness of the foil, one kind of high strength Al-1.2Mn alloy has been developed. In its fabrication process, the recrystallization structure after intermediate annealing greatly affects the surface topography of foil. In this study, the relationship between recrystallization structure during intermediate annealing after rolling and homogenization treatment conditions of Al-1.2Mn alloys has been investigated. Homogenization was carried out with one step treatment or two steps treatment. It was found that one step homogenization treated cold-rolling sheets had higher recrystallization temperature and finer complete recrystallization grains compared to two steps homogenization treated cold-rolling sheets. This phenomenon can be explained by the relationship between Mn precipitation and recrystallization behavior during intermediate annealing.

Introduction

In lithium ion secondary batteries, AA1070 & AA1085 aluminum alloy foils are widely used as cathode current collectors which act as electrical conductor as well as carrier of chemical substances such as $LiFePO_4$. For a battery with constant volume, the power capacity can be raised by increasing the amount of chemical substance through reducing the thickness of aluminum alloy foil. Nevertheless, the thin foil may be broken during coating process if its strength is not enough. So, it is very important to develop aluminum alloy foil with high strength and good electrical conductivity.

Addition of Mn is an effective method for obtaining high strength foil. This foil is fabricated generally by casting – homogenization - hot rolling - cold rolling - intermediate annealing - foil rolling. It is necessary to control the grain structures during intermediate annealing process because the structure greatly affects the surface topography of foil.

It is supposed that grain structure during intermediate annealing process varies from different homogenization conditions of Al-Mn series aluminum alloy due to different Mn content in solid solution. It is known that precipitates which formed prior to or during annealing have significant influence on nucleation and growth of the recrystallized grains, i.e. Zener pinning effect [1]. Several works have been carried out to investigate the relationship between precipitates and recrystallization behavior in Al-Mn alloys [2-8]. It is well described that recrystallization is prevented by the precipitation at low annealing temperature while it can complete before precipitation occurs at high temperature. Most of the former works were performed only with a single step homogenization to obtain supersaturated alloy. However, the precipitation of Mn-bearing precipitates can be quite different according to different homogenization conditions, which could lead to different effects on recrystallization behavior.

The objective of this study is to investigate the influence of homogenization conditions on the recrystallization behavior of Al-1.2Mn alloy sheets during intermediate annealing process in detail. The correlation between Mn precipitating and recrystallization behavior will be discussed.

Experimental Procedures

Preparation of Materials

The chemical composition of the Al-Mn alloy used in this study is listed in Table I. Ingots with gauge of 70 mm were made by direct chill casting (DC casting).

Table I. Chemical composition of the alloy used in the present study (mass %).

I.D.	Mn	Fe	Si	Ti	Al
Al-1.2Mn	1.20	0.21	0.22	0.01	Bal.

The ingot was homogenized by means of one step or two steps homogenization process, as shown in Figure 1.

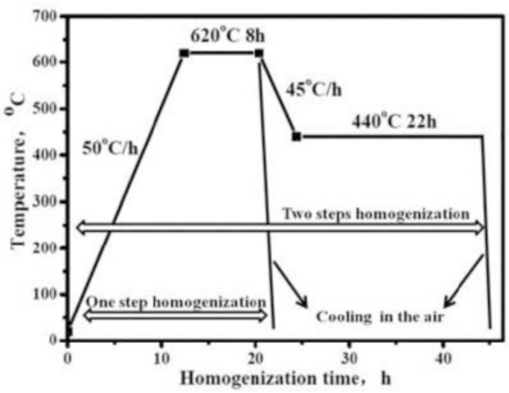

Figure 1. Details of homogenization processes used in the present study

After homogenization, the ingots were scalped to gauge of 50 mm, reheated to 440 °C and hot-rolled to 6 mm gauge, furthermore cold-rolled to 0.5 mm gauge sheets. Two different intermediate annealing processes were adopted after cold-rolling: batch annealing and salt bath annealing. The former was performed at 320 °C and 380 °C respectively for 4 hours in a batch furnace with heating rate of 30 °C/h and followed by air cooling, the latter was performed at 400 °C for 30 seconds in a salt bath with heating rate of about 100 °C/s and followed by water quenching.

Evaluation of Microstructures

The grain structure of longitudinal sections was observed by polarizing microscope after buff grinding and anodizing. After buff grinding and electrolyte polishing, intermetallic compounds were observed by optical microscopy, precipitates and grains were examined using electron channeling contrast (ECC) technique in SEM.

Measurement of Mn content in Solid Solution

Mn content in solid solution was estimated from the electrical resistivity by equation [9]:

$$\rho=2.7+2.94Mn_{ss}\%+0.34Mn_{pre}\%+2.56Fe_{ss}\%+0.058Fe_{pre}\%+1.02Si_{ss}\%+0.088Si_{pre}\% \quad (1)$$

Where $Mn_{ss}\%$, $Fe_{ss}\%$ and $Si_{ss}\%$ are the content of Mn, Fe and Si in solid solution, respectively. $Mn_{pre}\%$, $Fe_{pre}\%$ and $Si_{pre}\%$ are the content of Mn, Fe and Si precipitated from solid solution, respectively. In this study, electrical resistivity ρ_{alloy} was calculated from electrical conductivity by equation:

$$\rho_{alloy}(\mu\Omega\cdot cm) = 100/\kappa\ (MS/m) \quad (2)$$

Where κ means electrical conductivity which was measured by Sigma Test eddy conductivity apparatus after buff grinding.

As shown in equation (1), the influence of precipitated Fe and Si on electrical resistivity is very weak. Moreover, most of the Fe formed as intermetallic compounds during solidification, so the content of Fe in solid solution is very low. Si content in the present alloy is very low, too. The influence of Fe and Si contents change in solid solution on electrical resistivity during annealing could be ignored. Thus the change of electrical resistivity during intermediate annealing can be used to estimate the change of Mn content in solid solution by the following equation:

$$\triangle Mn_{ss}\% = (\rho_{before}-\rho_{after})/2.6 \quad (3)$$

Where ρ_{before} and ρ_{after} are the electrical resistivity before and after intermediate annealing. The change of Mn content in solid solution $\triangle Mn_{ss}\%$ also represents precipitated amount of Mn-bearing particles.

Results and Discussion

Microstructures of Ingots after Homogenization

Figure 2 shows microstructures of the alloy after one step and two steps homogenization, respectively. Large number of $Al_6(Fe,Mn)$ and $Al_{12}(Fe,Mn)_3Si$ intermetallic compounds form during solidification. For one step homogenization ingot only few AlMnSi precipitates can be observed since the temperature is high enough (620 °C) to dissolve large number of the precipitates which formed during the early stage of homogenization, as seen in Figure 2(a). However, as shown in Figure 2(b), high density of large AlMnSi precipitates with size of 0.5-1 μm can be observed in two steps homogenization ingot. This implies that AlMnSi phases precipitate and grow during cooling from 620 °C to 440 °C and keeping period at 440 °C.

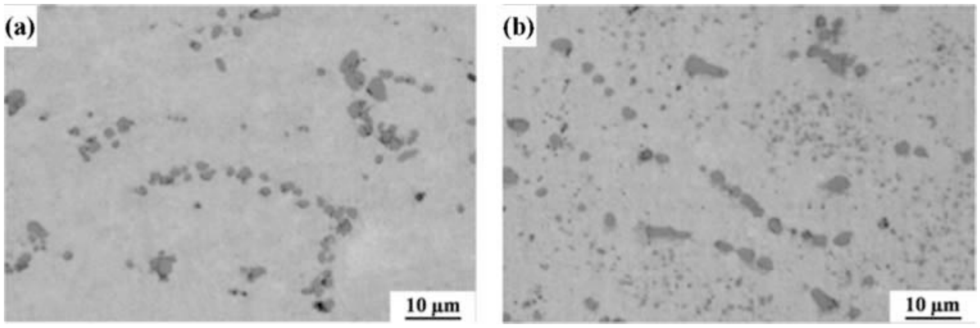

Figure 2. Microstructures of the alloy after: (a) one step homogenization and (b) two steps homogenization

Grain Structures of Sheets after Intermediate Annealing

Grain structures of the 0.5 mm gauge sheets annealed at 320 °C and 380 °C for 4 hours are shown in Figure 3. As annealed at 320 °C, recrystallization does not happen in the one step homogenization sheets, but recrystallization grains are observed in two steps homogenization sheets (Figure 3(a) and 3(b)). This implies that the recrystallization temperature is higher for one step homogenization sheets compared to two steps homogenization sheets. As annealing temperature raises to 380 °C, both sheets have completed recrystallization structures, grain size is smaller for one step sheets compared to two steps sheets (Figure 3(c) and 3(d)). Figure 4 shows grain structures of the sheets annealed at 400 °C for 30 seconds in salt bath, both one step and two steps homogenization sheets have the same fine grains. This means that heating rate affects the recrystallization behavior significantly.

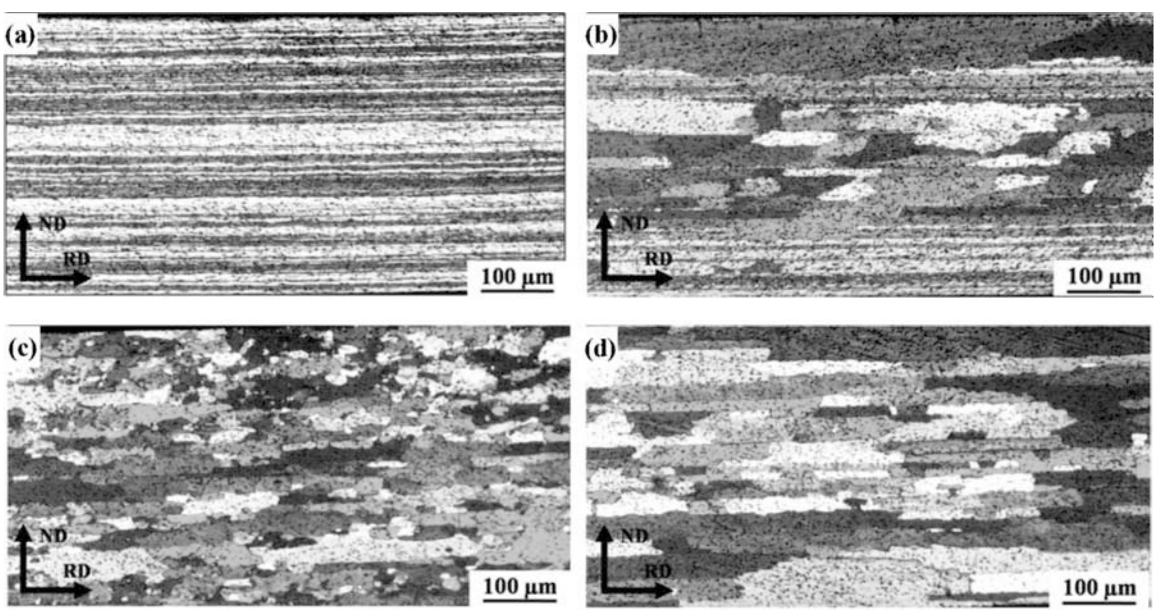

Figure 3. Grain structure after batch annealing :

(a) one step homogenization + 320 °C/4h, (b) two steps homogenization + 320 °C/4h,

(c) one step homogenization + 380 °C/4h, (d) two steps homogenization + 380 °C/4h

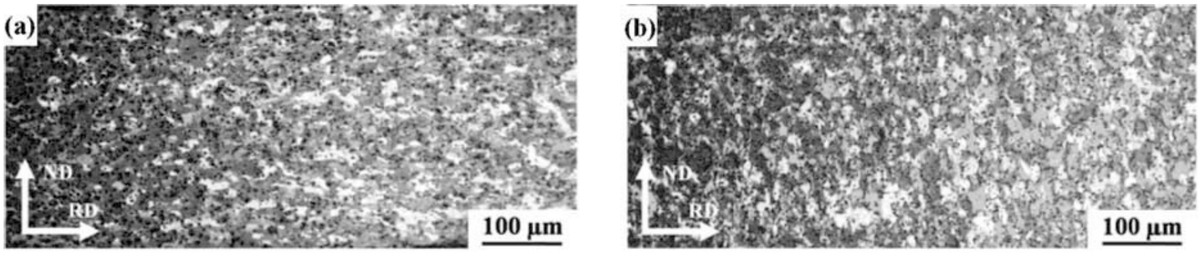

Figure 4. Grain structure after salt bath annealing: (a) one step homogenization+400 °C/30s, (b) two steps homogenization+400 °C/30s

Change of Mn in Solid Solution during Intermediate Annealing

Table II shows the variation of electrical resistivity of 0.5 mm gauge sheets with different intermediate annealing methods and corresponding change of Mn contents in solid solution $\triangle Mn_{ss}\%$ which estimated according to equation (3). It is clear that the electrical resistivity of cold-rolled sheets decreases after intermediate annealing. From the table, it is also clarified that more Mn was precipitated in one step homogenization sheets than two steps homogenization sheets during batch intermediate annealing (320 °C and 380 °C) because one step homogenization sheets has higher content of Mn in solid solution before annealing. Specially, one step homogenization sheets precipitates more Mn at 380 °C than 320 °C. However, when annealed by salt bath there is not much change in $Mn_{ss}\%$ for both one step and two steps homogenization sheets. This means that most of the Mn in solid solution does not have enough time to be precipitated during salt bath.

Table II. Electrical resistivity and $\triangle Mn_{ss}\%$ after different intermediate annealing conditions

		Cold-rolling	320 °C/4h (batch)	380 °C/4h (batch)	400 °C/30s (salt bath)
Electrical resistivity (μΩ·cm)	One step	5.03	3.94	3.60	4.88
	Two steps	4.13	3.52	3.56	4.05
$\triangle Mn_{ss}\%$ (mass%)	One step	-	0.42	0.55	0.06
	Two steps	-	0.22	0.18	0.03

Influence of Precipitates on Recrystallization Behaviors

Microstructures of the alloy sheets with two kinds of homogenization conditions after intermediate annealing at 320 °C are shown in Figure 5. Deformation structure is clearly observed after cold-rolling (CR) within both homogenization condition sheets, as shown in Figure 5(a) and 5(b). For one step homogenization sheets, only few precipitates can be observed compared to two steps homogenization sheets after cold-rolling. After intermediate annealing at 320 °C for 4 hours, many fine precipitates formed on the deformation structure within one step homogenized sheets. Those precipitates formed preferentially on subgrain boundaries and align along the rolling direction (RD), as shown in Figure 5(c). However, only very few precipitates is observed within two steps homogenization sheets after intermediate annealing (Figure 5(d)) and recrystallization occurs (Figure 3(b)).

It is well established that larger non-deformable particles (especially those larger than 1 μm) can promote recrystallization, i.e. particle stimulated nucleation (PSN) [10]. In the present study, PSN is assumed to be the dominant mechanism for recrystallization nucleation since most of the intermetallic compounds are larger than 1 μm after cold-rolling. For sheets with two steps homogenization, some of the precipitates grew to large size and thus could act as nucleation sites for recrystallization. Furthermore, from Figure 5 and Table II it can be seen that less precipitates formed during intermediate annealing in two steps homogenization sheets than in one step homogenization sheets. According to Nes [11], the precipitates with smaller size and higher density are more effective in inhibiting the movement of subgrain boundaries. Therefore the

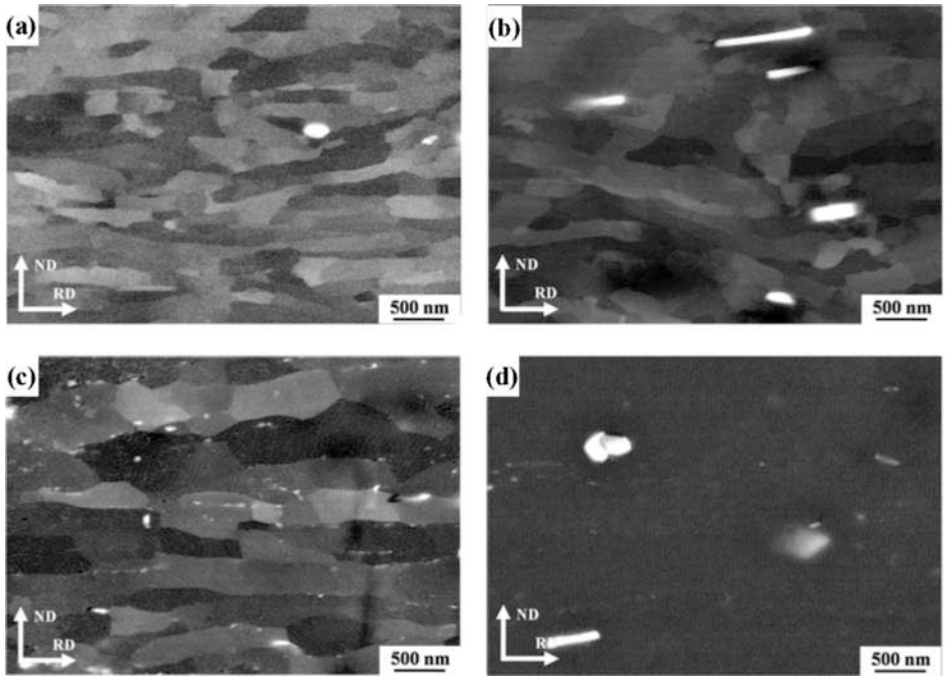

Figure 5 Microstructure of the alloy after:
(a) one step homogenization + CR, (b) two steps homogenization + CR,
(c) one step homogenization + CR + 320 ^{o}C/4h, (d) two steps homogenization + CR + 320 ^{o}C/4h

retarding from precipitates on recrystallization nucleation should be much weaker in two steps homogenization sheets than in one step homogenization sheets. This can explain that why one step homogenization sheets has a higher recrystallization temperature. Precipitates in the alloy inhibit not only nucleation but also growth of the recrystallized grains [12]. However, sheets annealed in salt bath show very similar grain structure between one step and two steps homogenization sheets, which indicating that the coarse precipitates formed during the second step homogenization do not have obvious effect on recrystallization. In one step homogenization sheets where more Mn-bearing precipitates formed during batch annealing, the growth of grains is effectively inhibited, which could result in relatively finer grain structure.

Conclusions

Influence of homogenization conditions on recrystallization behavior of Al-1.2Mn alloy used for lithium ion battery was investigated, the conclusions are as follows:

(1) Homogenization conditions affect recrystallization behavior of the Al-1.2Mn alloy sheets significantly during intermediate annealing. One step homogenization sheets had higher recrystallization temperature and finer complete recrystallization grain structure compared to two steps homogenization sheets.

(2) This phenomenon can be explained by relationship between Mn precipitation and recrystallization behavior during intermediate annealing. One step homogenization sheets had more Mn content in solid solution after cold-rolling and precipitated many fine particles during intermediate annealing, which retarded recrystallization behavior.

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