Study on the microstructures of Al-2.5%Mn alloy

Hang-qi Feng, Zhi-bo Yang, Ye-tong Bai, Li Zhang and Yu-lin Liu
School of Materials Science and Engineering, Shenyang Aerospace University, Shenyang 110136, People’s Republic of China
E-mail: ylliu@sau.edu.cn

Keywords: hypereutectic alloy, Sr element, modification, cooling rate

Abstract
The effect of Sr and cooling rate on the microstructure of Al-2.5%Mn alloy was studied by OM, SEM and XRD. The results showed that Sr not only refined the primary phase, but also refined the eutectic microstructure. However, there was obvious delamination in the alloy. When the content of Sr was 0.2%, the primary phase in the upper part of alloy changed from coarse needle and lath-shaped to fine block and needle-like. With the Sr content increased, the needle-like structure in the alloy tended to be more and longer, but the size of α-Al tended to be finer. At the bottom, there were many large massive phases, which were much more refined than the primary phase without Sr. With the cooling rate increased, the primary phase was refined greatly and almost all of them transformed into eutectic microstructure. Besides, the delamination of microstructure disappeared.

1. Introduction
In recent years, with the environmental protection and lightweight requirements improved, higher requirements are put for the comprehensive properties of materials. As an alloy with low strength but good elongation and corrosion resistance, Al–Mn alloy is used widely in the manufacture of automobile radiator. At present, in heavy trucks and other large vehicles, due to the poor operating environment, there are higher requirements for the strength, impact resistance and corrosion resistance of materials. At present, copper radiators are used mostly. Therefore, it is necessary to improve the strength and corrosion resistance of Al–Mn alloy in order to replace copper radiator [1–6].

The highest solid solubility of Mn in aluminum is 1.8 wt%, and the common content of Mn in Al–Mn alloy is 0.3 wt%–1.5 wt%. Adding too much Mn makes the Al–Mn alloy appear coarse microstructure and affect the properties of the alloy. However, increasing the content of Mn can not only improve the corrosion resistance, but also improve the strength. Therefore, how to increase the content of Mn and inhibit the formation of coarse microstructure is one of the research directions to expand the application of aluminum alloy [5, 7–14].

In recent years, domestic and overseas scholars have done a lot of researches on Al–Mn alloy. Luo et al [15] studied the effect of strong magnetic field on the microstructure of hypereutectic Al–Mn alloy (Al-5Mn). The results showed that the magnetic field had a regular effect on the microstructure of the alloy. With the magnetic field enhanced, the arrangement of Al<sub>6</sub>Mn compounds in the alloy was more regular. In addition, Al<sub>6</sub>Mn in the alloy would increase with the action time of strong magnetic field increased. Liu et al [16] have studied the influence of the addition of various alloying elements on the Al–Mn alloy. The results showed that the addition of an appropriate amount of Mg element in the Al–Mn alloy could promote the precipitation of AlMnSi phase, which was a dispersion phase favorable to the alloy performance. In addition, Zr and Ni elements would not only form high temperature resistant phases in the alloy, such as Al<sub>3</sub>Zr and AlMnSiNi, but also improved the high temperature resistance of the alloy. The types and quantity of precipitated phases in the alloy could also be increased. Liu et al [17] studied the effect of different manganese content (up to 2%) on the microstructure and high temperature properties of 3004 alloy. The results showed that when the content of Mn in the alloy was different, the types of compounds formed in the alloy were also different. When the Mn content was less than 1.5 wt%, the main compounds was Al<sub>6</sub> (MnFe). When the content of Mn reached 2 wt%, Al<sub>6</sub>Mn and a large number of fine Al<sub>6</sub> (MnFe) were the main components in the alloy. The quantity of coarse microstructure
increased rapidly and the quantity of fine microstructure decreased, which also led to the poor high temperature properties of the alloy. However, most studies have many limitations. For example, refinement was achieved by using special and expensive processes, which is a huge obstacle to the industrialization of hypereutectic Al–Mn alloys.

In our other study, we found that Sr element had refining effect on compounds containing Mn. Therefore, in this paper, Sr element was used to inhibit the formation of coarse microstructure in high Mn content alloy, so as to reduce the adverse effect caused by the increase of Mn content. The effect of cooling rate on the microstructure of the alloy was also studied. This study had a great impetus to the practical application of Al–Mn alloy with more than 1.6 wt%Mn content (maximum solid solubility is 1.8 wt%). It was helpful to improve the strength and application range of the alloy and had important application value and certain theoretical significance.

2. Experimental materials and methods

In this study, industrial pure aluminum, Al-10%Mn, and Al-10%Sr intermediate alloy were used as raw materials. The melting temperature was 720 °C. After the pure aluminum and Al-10%Mn was melted completely in the graphite crucible, Al-10%Sr was added and kept the temperature for 30 min, then mixed evenly. Then, the alloy liquid was poured into graphite mold and steel mold respectively for cooling, and the remaining alloy liquid was put into furnace for cooling. Finally, the alloy samples were analyzed by OM, SEM and XRD. The nominal chemical composition of the alloy in this experiment is shown in table 1.

3. Experimental results

3.1. Effect of Sr content on microstructure of alloy

As shown in figure 1, the microstructures of Al-2.5%Mn alloy with different Sr content was shown. It could be seen clearly that when the Sr content was 0%, the microstructure in the alloy was thick strip and block, and the size could reach millimeter level. However, when the Sr content was 0.2%, the thick strip and needle like microstructures disappeared and became fine block microstructures and eutectic microstructures. When the content of Sr increased to 0.35%, the microstructures of the alloy was further refined, and the fine block microstructures disappeared. The microstructures of the alloy became completely eutectic microstructures, and the grain size was also reduced significantly, the refining effect was the best. With the further increase of Sr content (0.5% and 0.65%), it could be seen that there was a needle like microstructures in the alloy, and the number and size of needle like microstructures were increased with the increase of Sr content. Although the increase of Sr content refined the microstructures of the alloy, it was generally considered that the needle like microstructures was not good for the comprehensive properties of the alloy, so excessive Sr content would bring bad effects. In addition, Sr not only improved the morphology of the coarse primary phase, but also refined the eutectic microstructures in the alloy.

As shown in figure 2, it could be seen from the enlarged metallographic pictures that there were two kinds of microstructures in the alloy, one was fibrous eutectic microstructures, the other was needle like eutectic microstructures. With the addition of 0.35% Sr, the needle like microstructures appeared obviously, and with the increase of Sr content, the number and size of needle like microstructures also increased, but the grain size of the alloy reduced obviously. In a word, the best effect was 0.35% Sr.

During the pouring of Al-2.5%Mn-0.35%Sr alloy thick plate, it was found that some coarse microstructures still appeared in the alloy, which influenced the properties of the alloy. After analysis, the stratification phenomenon was found (figure 3). When the Sr content was 0% (figure 3(a)), the coarse microstructure in the alloy was dispersed without centralized distribution. However, when 0.35% Sr was added (figure 3(b)), the microstructure in the alloy showed obvious stratification, the upper part was all eutectic microstructure, the

| No. | Mn   | Sr  | Al  |
|-----|------|-----|-----|
| 1   | —    | —   | bal |
| 2   | 0.20 | 0.35| bal |
| 3   | 2.5  | 0.35| bal |
| 4   | 0.50 | —   | bal |
| 5   | 0.65 | —   | bal |
bottom was relatively coarse massive phase, and the height of the bottom precipitation layer was about 5 mm. In addition, compared with the coarse microstructure in Al-2.5%Mn alloy, the bulk phase deposited at the bottom was much finer, and the edge of the precipitated phase tended to spheroidize. This morphology could reduce greatly the harmful effect on the alloy. Figure 3(b) showed that there were some long microstructures in the upper part of the alloy, but this kind of microstructure was a coarser eutectic microstructure with less damage. After scanning by SEM, it was found that the fibrous structure in the upper part of the alloy was the phase containing Al and Mn elements, while the short rod structure was the phase containing Al and Sr elements. Figure 4 showed the surface distribution of Mn and Sr in Al-2.5%Mn-0.35%Sr alloy.

Then took samples of size $15 \times 15 \times 5$ mm at the bottom and top of the Al-2.5%Mn-0.3%Sr alloy respectively. Observed the metallography to ensure that the samples were typical top microstructure and bottom precipitate microstructure. Then carried out XRD test, scanning angle was $10^{\circ} - 90^{\circ}$, scanning time was 14 min. As shown in figure 5(a), combined with XRD analysis of the above sample, it was found that there were mainly $\text{Al}_4\text{Sr}$ and $\text{Al}_6\text{Mn}$ phases in the upper part of the alloy. Therefore, combined with SEM surface distribution and XRD analysis, it could be seen that the short rod and fine needle structures were $\text{Al}_6\text{Sr}$ phases and the fibrous structures were $\text{Al}_4\text{Mn}$ phases. According to the XRD analysis of figure 5(b), except $\alpha$-Al, it could be seen that the

![Figure 1. Microstructure of Al-2.5%Mn furnace cooled alloys with different Sr contents on the upper part: (a) 0%, (b) 0.2%, (c) 0.35%, (d) 0.5%, (e) 0.65%.

---

**Figure 1.** Microstructure of Al-2.5%Mn furnace cooled alloys with different Sr contents on the upper part: (a) 0%, (b) 0.2%, (c) 0.35%, (d) 0.5%, (e) 0.65%.
bottom of alloy was all Al₆Mn phase, so the bulk structures at the bottom were Al₆Mn. In addition, a large number of the bulk structures concentrated at the bottom could be removed selectively.

3.2. Influence of cooling rate on Al-2.5%Mn-0.35%Sr alloy

As shown in figure 6(a), the morphology of precipitation at the bottom of the alloy was clearly visible and there was no other microstructure in the furnace cooling. As shown in figure 6(b), when air-cooled, the fibrous and short rod-like structures in the alloy were refined obviously, and the size of α-Al decreased obviously. Due to the refinement of the microstructures, the number of eutectic microstructures was further increased, and there were a small amount of non-eutectic massive phase. The fibrous and short rod-like structures in the alloy were further refined, the size of α-Al was smaller, and the number of eutectic structures was further increased under the iron mold cooling in figure 6(c). Under the condition of steel mold cooling, there were also a small amount of small block phase, which cannot achieve complete eutectic, but its volume was smaller than air cooling and furnace cooling.

As shown in figure 7, it could be observed that with the cooling rate increased, the scale of α-Al decreased significantly, the short rod and fibrous microstructures were also smaller and smaller, and there was a small amount of small block microstructures in the air cooling and steel mold cooling after magnification. The obvious refinement of microstructure and grain was beneficial to the mechanical properties of the alloy. This showed that the addition of Sr was beneficial to the eutectic of the alloy. After increasing the cooling rate, there was no delamination in the sample.

4. Analysis and discussion

4.1. Effect of Sr content

The ternary phase diagram of Al–Mn–Sr showed that the alloy would not form AlMnSr compounds at 705 °C melting temperature (figure 8(a)). Therefore, no AlMnSr compound was detected in Al-2.5%Mn-0.35%Sr alloy.

The binary phase diagram of Al–Sr showed Al₄Sr is formed mainly during the preparation of Al-10%Sr master alloy (figure 8(b)). The melting point of Al₄Sr compounds is high. Only when the melting temperature is
higher than 1000 °C, can complete liquid be formed. According to the binary phase diagram of Al–Mn, the melt of the alloy still exists in the form of L + Al4Mn or L + Al6Mn at temperatures below 820 °C.

Therefore, free AlMn atomic group or fine Al4Mn compounds were uniformly present in Al-2.5%Mn alloy melt during melting at 705 °C (figure 9(1)). When Al-10%Sr was added to the melt, Sr-containing compounds or larger atomic group, were released into the melt, such as Al4Sr. These compounds or atomic group would preferentially bind to AlMn atomic group or compounds. A layer of AlSr atomic group surrounded the AlMn atomic group (figure 9(2)), which further enlarged the size of the atomic group, increased the effective nucleation core, and achieved the refinement effect. Because the d-electron layer of Mn is not full, it is easier to bind with Al than Sr. Therefore, the AlMn atom layer would be surrounded again outside the AlSr layer, and grewed continuously to form Al6Mn compounds (figure 9(3)). These Al6Mn compounds showed bulk and fibrous morphology (figure 9(4)). The proportion of these grown bulk Al6Mn was larger, and the solidification

![Figure 3](image3.png)

Figure 3. Distribution of microstructure after adding 0.33% Sr in furnace cooling: (a) Al-2.5%Mn, (b) Al-2.5%Mn-0.33%Sr and (c) Bottom microstructure.

![Figure 4](image4.png)

Figure 4. Plane distribution of Mn and Sr element in No. 3 alloy.
speed of the alloy is very slow under furnace cooling. These Al$_6$Mn phases had enough time to sink to the bottom of the alloy (Figure 9(5)) and form precipitation (Figure 9(6)). At the same time, due to the high preparation temperature of Al-10Sr, there will be a certain number of high melting point AlSr compounds in the alloy. The release of these compounds will also become the nucleation core of the alloy solidification, which will greatly increase the nucleation rate of the alloy and also provide the core for the formation of AlMn phase. At the same time, because Al$_4$Sr compounds began to form in large quantities, the distribution of these compounds also had a certain impact on the morphology of AlMn compounds, making AlMn compounds appear fibrous.

At the same time, Al$_4$Sr formed by Sr addition also provided heterogeneous nucleation core for $\alpha$-Al, refined the grain of $\alpha$-Al, and refined the grain of the alloy. With the increase of Sr content, the amount of Al$_4$Sr formed in alloy solution was also increased. Therefore, with the increase of Sr content, the size of $\alpha$-Al became smaller.
and smaller. When the nucleation reaches the limit, the grain size of $\alpha$-Al does not decrease any more, but exists in the microstructure of the alloy as a single compound.

### 4.2. Effect of cooling rate

The relationship between nucleation rate and temperature:

$$I = I_0 \exp \left(- \frac{\Delta G_n^* + \Delta G_d}{kT} \right)$$

where $I$ is the nucleation rate, $I_0$ and $k$ are constants, $\Delta G_n^*$ is the nucleation energy, $\Delta G_d$ is the diffusion activation energy, and $T$ is the temperature.
Non-spontaneous nucleation energy expression:

$$\Delta G^* = \frac{16\pi\sigma^3}{3\Delta G_m^2} f(\theta)$$

Where $\Delta G^*$ is the non-spontaneous nucleation energy, $\Delta G_m$ is Gibbs free energy difference of unit mole of solid and liquid, $\sigma$ is the interface energy, and $\theta$ is the wetting angle.

The study results showed that the value of $f(\theta)$ has nothing to do with the mold in the same alloy. Therefore, the relationship between $I$ and $T$ shown in Figure 10 shows that the lower the supercooling, the higher the nucleation energy required for non-spontaneous nucleation and the lower the nucleation rate. The higher the supercooling, the smaller the non-spontaneous nucleation energy and the higher the nucleation rate required. Therefore, with the cooling rate increased in different molds, the supercooling degree of alloy liquid increased and the nucleation rate of alloy increased. At the same time, the nucleation and growth of Al–Sr compound formed in the early stage of crystallization provided heterogeneous core. So they had a positive impact on the size and morphology of microstructure and grain [18, 19]. At the same time, the solidification rate of the alloy increased obviously with the increase of cooling rate. Therefore, the phenomenon of gravity segregation could
not occur. In addition, the bulk phase had been further refined obviously and the adverse effect on the alloy would be greatly reduced.

It could be seen that the increase of cooling rate was very beneficial to the properties of the alloy from the change of microstructure. Since Al–Mn alloy belongs to the non-heat treatment strengthening alloy, the subsequent strengthening measures such as deformation strengthening will be taken. Therefore, the problem that the primary phase did not have enough time to sink due to the increase of cooling rate will be further reduced by the subsequent process of crushing.

5. Conclusion

(1) The size and morphology of the microstructure of Al–Mn alloy were improved significantly by Sr. After adding Sr, much eutectic structure appeared in the upper part of the alloy. When the Sr content was more than 0.35%, all the upper parts of the alloy were eutectic structure.

(2) Although Sr had a good effect, delamination occurred in the furnace cooling, which was mainly due to gravity segregation. The delamination could be eliminated by increasing the cooling rate.

(3) The addition of Sr could promote the eutectic of the alloy. When the cooling rate increased, the microstructure was refined obviously and became eutectic microstructure basically.

ORCID iDs

Hang-qi Feng https://orcid.org/0000-0002-5007-6156

References

[1] Chen Z, Xie B and Fan Q 2018 Formation and microstructure of quasicrystals in suction cast Al–6 wt% Mn alloys with additions of nickel and iron elements Materialwiss. Werkstofftech. 49 1236–44
[2] Huang X H, Zuo X R and Wang Q W 2009 Research present situation of Al–Mn alloys World Nonferrous Metals 1 38–9
[3] Zhen L, Zhan Z and Grant C X 2018 Improvement in the mechanical properties and creep resistance of Al–Mn–Mg 3004 alloy with Sc and Zr addition Materials Science and Engineering: A 729 196–207
[4] Chen X P, Mei L, Li S and Shang L M 2018 Effects of homogenisation treatment on microstructure and grain refinement of Al–1.2Mn alloy Mater. Sci. Technol. 34 493–501
[5] Hu T et al 2018 Evolution of microstructure in Al–Mn alloy with a low ratio of Fe/Si during homogenization Rare Met. Mater. Eng. 47 2631–6
[6] Cao C et al 2019 Improved strength and enhanced pitting corrosion resistance of Al–Mn alloy with Zr addition Mater. Lett. 255 126535
[7] Maied H and Cai W 2017 The effects of Mn concentration on the tribocorrosion resistance of Al–Mn alloys Wear 380–381 191–202
[8] Liu Y L et al 2016 Effect of Fe, Si and cooling rate on the formation of Fe- and Mn-rich intermetallics in Al–5Mg–0.8Mn alloy Journal of Materials Science & Technology 32 305–12
[9] Huang K and Marthinsen K 2015 The effect of heating rate on the softening behaviour of a deformed Al–Mn alloy with strong and weak concurrent precipitation Mater. Charact. 110 215–21
[10] Liu X C et al 2017 Microstructure control and high temperature performance of Al–Mn alloys Acta Metall. Sinica 53 78–85
[11] Liu K et al 2017 Influence of TiB2 nanoparticles on elevated-temperature properties of Al–Mg–Mn 3004 alloy Transactions of Nonferrous Metals Society of China 27 771–8
[12] Kula A, Blaz L and Lobry P 2016 Structure and properties studies of rapidly solidified Al–Mn alloys Key Eng. Mater. 682 199–204
[13] Zhang J C et al 2014 Effect of Zr addition on microstructure and properties of Al–Mn–Si–Zn-based alloy Transactions of Nonferrous Metals Society of China 24 3872–8
[14] Li Z, Zhang Z and Chen X G 2016 Effect of magnesium on the dispersion phase of Al–Mn–Mg–Si(3xxx) alloy dispersion Transactions of Nonferrous Metals Society of China 6–12
[15] Luo D W et al 2009 Effect of high magnetic fields on the solidification microstructure of an Al–Mn alloy Rare Met. Mater. Eng. 28 302–8
[16] Liu X C et al 2017 Microstructure control and high temperature properties of Al–Mn-based alloys Acta Metall. Sinica 53 1487–94
[17] Liu K and Chen X 2017 Evolution of microstructure and elevated-temperature properties with Mn addition in Al–Mn–Mg alloys J. Mater. Res. 32 1–9
[18] Feng H Q et al 2019 Effect of Cr content and cooling rate on the primary phase of Al-2.5Mn alloy Int. J. Miner. Metall. Mater. 26 1551–8
[19] Zhang Y et al 2018 Effect of cooling rate on solidification structure of Mg–_8Gd–1Er alloy Rare Met. Mater. Eng. 47 3120–6