Effects of thermal-rate treatment and modification of Ce on the microstructure and properties of A356 alloys

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Abstract. In this study, the effects of thermal-rate treatment (TRT) and modification of Ce on the microstructure and mechanical properties of A356 alloy were investigated. The results showed that the microstructure of A356 alloy was improved after TRT and modification of Ce. The α-Al was refined significantly and the eutectic Si transformed from needle-like shape to granular-like shape. When the content of Ce increased to 0.5%, the grain size of α-Al of A356 alloy began to increase and the dendrites became coarse. When the Ce content was 0.4%, the tensile strength and yield strength of A356 alloy were 183MPa and 124 MPa, respectively. The mechanism of (TRT+Ce) on the grain refinement of α-Al and modification of eutectic Si was discussed.

1. Introduction

A356 alloy has excellent comprehensive properties such as good fluidity, small shrinkage and low tendency of hot cracking, which can be widely used in aerospace, automobile and other fields. The morphology and distribution of primary α-Al and eutectic Si phase in A356 alloy determine its mechanical properties [1-5]. Usually, the primary α-Al is coarse dendrite and the needle-like eutectic Si distributes around the α-Al unevenly in the A356 alloy, which could reduce the mechanical properties, thus greatly limiting the application of A356 alloy. Traditionally, the refiners or modifiers such as Al-Ti-B, Al-Ti-C, Al-Ti-B-N and rare earth etc are usually used to refine the α-Al or modify the eutectic Si phase in Al-Si alloys, thereby improving the microstructure and strengthen the mechanical properties [6-8].

Many previous results have confirmed that the solidification microstructure of alloy is not only related to the solidification process, but also directly related with the melt structure and thermal history of alloy [9-11]. According to heredity theory, there are a lot of clusters in metal or alloy melts, and the melt temperature has a great influence on the clusters in the melt. The higher the melt temperature is, the smaller the size of ordered clusters is. Therefore, the alloy melt has non-uniform metastable characteristic in the solidification process, which is considered to be inherited from the master melt. The short-term non-uniform phenomenon of melt structure is of great significance for the melt treatment of alloy. Taking advantage of it, some techniques of melt treatment such as superheating...
treatment, heat/cold cycle and thermal-rate treatment, have been developed for improving the solidification structure. Thermal-rate treatment (TRT) is one of method of melt treatment. Usually, the melt is first superheated to a certain higher temperature, which is higher than its liquidus and then cooled quickly to a pouring temperature before pouring [12-14]. During the solidification process, the fine and uniform microstructure in alloy melt could be retained, resulting in the improvement of microstructure and mechanical properties. So far, there are few reports about TRT in as-cast A356 alloy.

In this study, the effects of TRT and modification of Ce on the microstructure and mechanical properties were investigated. The mechanism of (TRT+Ce) on the grain refinement of $\alpha$-Al and modification of eutectic Si was discussed. It is expected to provide a useful guidance for the preparation and application of A356 alloy.

2. Experimental procedures

The proportioned commercial pure Al ingot (99.9 wt.%), pure Zn ingot (99.99 wt.%), Mg ingot (99.7 wt.%), Fe block (99.99 wt.%), Cu block (99.99 wt.%), and Ti block (99.998 wt.%) were used to prepare the pre-prepared alloy in the electrical resistance furnace. The heating rate was set as 10 °C/min. The pre-prepared alloy was first melted at 900°C and kept for 30 min. Then the chill ingot (the ratio of chill ingot to the melt is 1/3) were added into the melt to make sure the temperature of alloy melt dropped rapidly to 660 °C. Modification treatments were carried out with the addition of Al-20%Ce master alloy and the alloy was held at 660°C for 5 min after thermal-rate treatment (TRT). Finally, the alloy melt was poured into the permanent mold.

The constituent phases of A356 alloys were identified by an X-ray diffraction (XRD, Bruker D8 Advance) with Cu Ka operated with a voltage of 36 KV. The microstructure and phase composition of A356 samples were examined under a scanning electron microscope (SEM, JEOL, JXA-8100, Tokyo, Japan) equipped with an energy-dispersive spectrum. Differential scanning calorimetry (DSC) experiment was performed in pure argon atmosphere using the differential scanning calorimeter (DSC, Mettler-Toledo, Zurich, Switzerland) at a heating rate of 10 °C/min in the temperature range of 25 °C - 950 °C. The tensile properties of A356 specimens were carried out at room temperature using a universal testing machine (WDW-100A) at a constant rate of 5 mm/min.

3. Results and Discussion

3.1. DSC analysis

Figure 1 shows the DSC results of A356 alloy. It can be seen that there was an endothermic peak at 600 °C, which should be related with the melting of eutectic structure in the aluminum alloy during the heating process. In addition, a very small exothermic peak can be observed in the temperature range from 862 °C to 886 °C, just as shown in the illustration of Figure 1. As there is no other phase transformation in this temperature range, the exothermic peak should correspond to the liquid structural change of aluminum alloy melt. When the temperature of alloy melt changes, the bond distance (Al-Al, Al-Si and Si-Si) and atom distribution in some clusters of melt could change greatly.

Dahlborg et al measured the hydrogen concentration of aluminum alloy melt and confirmed that there was a partial liquid structure change in the aluminum alloy melt when the temperature reached 780 °C [15]. Lots of experimental studies also confirmed that there is a liquid structural transition region of Al melt in the temperature range from 780 °C to 930 °C [16-19]. Therefore, the liquid structure change occurred in A356 alloy melt between 862 °C and 886 °C and the temperature of TRT was set as 900 °C.
3.2. XRD analysis and microstructure

Figure 2 shows the XRD diffraction patterns of A356 alloys after TRT and modification of Ce. It can be seen that the A356 alloys mainly consisted of Al phase and Si phase. After TRT and modification of Ce, there were no diffraction peaks of TiAl₃ and Mg₂Si phases in the alloy. As the addition of Ce was tiny, no AlCe₃ was detected. However, when the addition of Ce reached 0.5%, some weak Al₃Ce peaks appeared in the XRD patterns.

According to the Al-Si binary phase diagram, the α-Al phase first nucleates, grows and then gradually solidifies into the dendrites in the solidification of A356 alloy. Figure 3 shows the microstructure of as-cast A356 alloy after TRT and modification of Ce. It can be observed that the primary α-Al was coarse dendrite and the primary dendrite size was more than 200 μm for the as-cast A356 alloy without the addition of Ce and thermal rate treatment. After TRT and the addition of 0.2% Ce, the primary dendrites of α-Al decreased obviously. With the addition of Ce increasing, the primary dendrites became equiaxed and the secondary dendrites began to decrease obviously, just as shown in Figure 3(c) and Figure 3(d). When the addition of Ce was 0.4%, the morphology and size of α-Al reached the optimal state. When the content of Ce reached 0.5%, the grain size of α-Al increased obviously and the dendrite became coarse, just as shown in Figure 3(f).
Figure 4 shows the morphology of eutectic Si of as-cast A356 alloy after TRT and modification of Ce. It can be seen that the eutectic Si of A356 alloy without any treatment was in the form of needle or block and distributed unevenly, just as shown in Figure 4(a). After thermal rate treatment and the addition of 0.2%Ce, the length of eutectic Si was significantly reduced. Although the distribution of eutectic Si was relatively concentrated, it showed a trend of becoming short rod. Furthermore, with the addition of Ce increasing, the eutectic Si became short-rod or granular and distributed uniformly on the grain boundary of α-Al, as shown in Figure 4(c) and Figure 4(d). However, when the Ce content was 0.45%, as shown in Figure 4(e), eutectic Si began to grow up and changed from fine particles to short rods. When the addition of Ce was 0.5%, it can be seen that eutectic Si continued to grow and changed from short-rod shape to needle. In addition, the aggregation phenomenon occurred and some eutectic Si had obvious sharp angles, just as shown in Figure 4(f).

![Fig. 3. Microstructure of as-cast A356 alloy after TRT and modification of Ce; (a) A356 without TRT; (b) 0.2%Ce; (c) 0.3%Ce; (d) 0.4%Ce; (e) 0.45%Ce; (f) 0.5%Ce.](image-url)
Fig. 4. Morphology of eutectic Si of as-cast A356 alloy after TRT and modification of Ce; (a) A356 without TRT; (b) 0.2%Ce; (c) 0.3%Ce; (d) 0.4%Ce; (e) 0.45%Ce; (f) 0.5%Ce.

Figure 5 shows the SEM and element distribution of as-cast A356 alloy after thermal rate treatment and the addition of 0.2%Ce. It can be further seen that the $\alpha$-Al dendrites were refined obviously and the eutectic Si phase with needle-like shape began to transform into short-rod shape. In addition, the distribution of Ce was consistent with that of Si phase, which was mainly distributed at the grain boundary of $\alpha$-Al.

Fig. 5. SEM and element distribution mapping of as-cast A356 alloy after after TRT and the addition of 0.2%Ce.
3.3. Analysis of solidification behaviours

Figure 6(a) shows the cooling curve of typical alloy, where $T_E$ is the eutectic temperature, $T_G$ is the recalescence temperature, $T_N$ is the nucleation temperature, $T_M$ is the start temperature of solidification, and $\Delta T = T_E - T_M$ is the undercooling degree. Generally, $\Delta T_{EG}$ is considered to be one of the best parameters to characterize the Si modification grade [20-22]. The larger the $\Delta T_{EG}$ is, the higher the Si modification grade is. Figure 6(b)-(d) show the cooling curves of A356 alloys treated by different solidification process, which the normal solidification (NS) and TRT were carried out at room temperature. Table 1 lists the solidification parameters of different process for A356 alloys. It can be seen from Table 1 that the $\Delta T$ of A356 alloy was enhanced to after TRT and modification of Ce. According to the classic nucleation theory, the critical nucleus radius can be expressed by

$$r_k = \frac{2\sigma T_m}{\Delta H_f \Delta T}$$

(1)

where $r_k$ is the critical nucleus radius, $\sigma$ is the surface energy per unit area, and $\Delta H_f$ is the latent heat of melting. With the increase of $\Delta T$, $r_k$ and nucleation work decrease, which makes the nucleation easier. On the other hand, when the $\Delta T$ is large, the diffusion and migration of atoms in the melt are difficult which result in the slow growth rate of grains [23-25]. It can be seen from Table 1 that the $\Delta T_{EG}$ of A356 alloy after TRT was larger than that of A356 alloy after NS, indicating that TRT can play a better role in Si modification and grain refinement, which was consistent with the Si morphology in Figure 4. When the $\Delta T_{EG}$ of A356 alloy reached 12.2°C after TRT and modification of Ce, the modification grade of Si phase in A356 alloy was the highest, suggesting that the TRT and the addition of Ce had the best modification effect on hypoeutectic Al-Si alloy, and the microstructure of A356 alloy was improved obviously.

![Fig. 6. The cooling curves of A356 alloys treated by different solidification process; (a) typical cooling curve; (b) NS; (c) TRT; (d) TRT+0.4%Ce.](image)

Table 1. Solidification parameters of different process for the A356 alloys.

| Process | $T_m/°C$ | $T_o/°C$ | $\Delta T/°C$ | $\Delta T_{EG}/°C$ |
|---------|---------|---------|--------------|-----------------|
| NS      | 571.7   | 574.8   | 9.3          | 6.2             |
| TRT     | 568.6   | 572.7   | 12.4         | 8.3             |
As is well known, the higher the temperature of alloy melt, the smaller the average size of atom clusters in the melt. The difference of melt temperature and composition could cause the structure change of melt. Therefore, the atom clusters existing in the melt have a certain probability to nucleate during solidification. With the increase of melt temperature, the larger size clusters in the melt disappear and the melt presents a uniform state. In the process of TRT, the cold metal was added into the melt and the temperature of melt decreased in a short time. According to the heredity of liquid metal, the small cluster structure of melt can be retained in the solidification microstructure, resulting in the grain refinement of alloy. In addition, the addition of chilling ingot can increase the local cooling rate of melt, refine the primary dendrite of $\alpha$-Al and improve the as-cast microstructure and mechanical properties of A356 alloy. On the other hand, Ce usually existed in the front of the solid/liquid interface due to the limited solubility of Ce in $\alpha$-Al, which could increase the compositional undercooling of alloy and decrease the growth rate of $\alpha$-Al, leading to the grain refinement of A356 alloy.

### 3.4. Mechanical properties

Figure 7 shows the tensile strength and yield strength of as-cast A356 alloy after different process. Compared with the tensile strength and yield strength of A356 alloy without TRT, the tensile strength and yield strength of A356 alloy after TRT were greatly improved. The tensile strength and yield strength of A356 alloy after TRT were 170 MPa and 112 MPa respectively, which were 5.6% and 6.7% higher than those of A356 alloy without TRT. In addition, the elongation of A356 alloy after TRT was slightly increased, which was 5.8%, as shown in Figure 8. Due to the grain refinement of $\alpha$-Al resulting from TRT, the mechanical properties were enhanced. It is also can be seen that the tensile strength and yield strength of A356 alloy first increased and then decreased with the increase of Ce content. When the addition of Ce was 0.4%, the tensile strength and yield strength of A356 alloy were 183 MPa and 124 MPa, respectively. When the Ce content continued to increase, the tensile strength began to decrease slowly, which should be mainly related with change of grain size of $\alpha$-Al and the morphology of eutectic Si, as shown in Figure 3 and Figure 4. The elongation of A356 alloy decreased with the increase of Ce content in the process of TRT and the elongation of A356 alloy treated by (TRT+ 0.4%Ce) was 4.6%.

| TRT+0.4%Ce | 565.9 | 568.8 | 15.1 | 12.2 |

Figure 7. The tensile strength and yield strength of as-cast A356 alloy after TRT and modification of Ce.
4. Conclusions
There was an exothermic peak between 862 °C and 886 °C in the DSC curve of A356 alloy, which corresponded to the liquid structural change of A356 alloy melt. The microstructure of A356 alloy was improved after TRT and modification of Ce. The $\alpha$-Al was refined significantly and the eutectic Si transformed from needle-like shape to granular-like shape. With the increase of Ce, the dendrites of $\alpha$-Al of A356 alloy gradually changed from coarse dendrites to equiaxed dendrites and the secondary dendrites decreased obviously. When the content of Ce increased to 0.5%, the grain size of $\alpha$-Al began to increase and the dendrite became coarse. The tensile strength and yield strength of A356 alloy increased first and then decreased with the increase of Ce content. When Ce content was 0.4%, the tensile strength and yield strength of A356 alloy were 183MPa and 124 MPa, respectively.

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References
[1] G. Evangelia, A. Michael, G. Gkantou, S. Kamaris, Eng. Struct 227, 111372 (2021)
[2] W.W. Ding, X.Y. Zhao, T.L. Chen, H.X. Zhang, X.X. Liu, D.K. Lei, J. Alloy. Compd 830, 154685 (2020)
[3] Q.J. Zheng, L.L. Zhang, H.X. Jiang, J.Z. Zhao, J. He, J. Mater. Sci. Technol 47, 142 (2020)
[4] G. Ridvan, A. Serhat, K. Alptekin, A.G. Kerem, K. Ahmet, T.Nonferr. Metal. Soc 28, 385 (2018)
[5] K. Zhao, T. Gao, H.B. Yang, G.L. Liu, J. Alloy. Compd 820, 153089 (2020)
[6] L.I. Ming, L.I. Yuan, L. Guan, H. Xiao, C. Ti, M. Ying, T. Nonferr. Metal. Soc 28, 393 (2018)
[7] M. Joel, X. Anthony, Mater. Today 5, 13556 (2018)
[8] Z.M. Shi, Q. Wang, Y.T. Shi, G. Zhao, R.Y. Zhang, J. Rare. Earth 33, 1004 (2015)
[9] E.M. Amne, S.G. Shabestari, T. Nonferr. Metal. Soc 26, 956 (2016)
[10] M. Marzouk, M. Jain, S. Shankar, Mat. Sci. Eng. A 598, 277 (2014)
[11] S.C. Wang, N. Zhou, W.J. Qi, K.H. Zheng, T. Nonferr. Metal. Soc 24, 2214 (2014)
[12] L.Y. Zhang, Y.H. Jiang, S.F. Shan, Y.Z. Ji, C.Z. Fan, W.K. Wang, J. Mate. Process. Tech 207, 107 (2008)
[13] Y.Y. Dong, C.S. Zhang, G.Q. Zhao, Y.J. Guan, A.J. Gao, Mater. Design 92, 983 (2016)
[14] A.F. Muhammad, X. Cong, X.J. Wang, S.J. Han, Y. Hiroshi, Mat. Sci. Eng. A 604, 122 (2014)
[15] U. Dahlborg, M. Besser, D.M. Calvo, J. Non-Cryst. Solids 353, 3005 (2007)
[16] Y. Kita, J.B. Zytveld, Z. Movrita, T. Iida, J. Phys-Condens. Mat 33, 811 (1994)
[17] P. Jia, X.L. Li, J.Y. Zhang, X.Y. Teng, X. Hu, C. Yang, D.G. Zhao, J. Mol. Liq 263, 218 (2018)
[18] L. Wang, L. Bo, Y.P. Wang, D. Wu, P. Jia, M. Zuo, D.G. Zhao, J. Mol. Liq 263, 349 (2018)
[19] L. Bo, S.S. Li, L. Wang, D. Wu, M. Zuo, D.G. Zhao, *Results. Phys* 8, 1086 (2018)
[20] T. Hiroyuki, N. Takanori, U. Kentaro, S. Yoshio, K. Masakazu, *Acta. Mater* 58, 2014 (2010)
[21] J.H. Jeon, J.H. Shin, D.H. Bae, *Mat. Sci. Eng. A* 748, 367 (2019)
[22] G. Heiberg, L. Arnberg, J. Light. *Metals* 1, 43 (2001)
[23] L. Aguilera, H. Manch, M.J. Molinarb, R. Castro, B. Escobedo, T. Herrera, *T. Mat. Sci. Eng. A* 561, 1 (2013)
[24] S.M. Venkatesan, X. Anthony, *Mater. Today* 5, 11175 (2018)
[25] A. Muhammad, G. Khaled, T.R. Majid, V. Ana, *J. Mater. Res. Technol* 9, 12484 (2020)