THERMAL RATE TREATMENT AND ITS EFFECT ON MODIFICATION OF Al-Si ALLOYS①

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ABSTRACT A new melting technique– Thermal Rate Treatment (TRT) has been studied in connection with Al-Si based alloys. TRT technique obviously improves the impact toughness of the alloys, refines the primary Si phase and increases the amount of the α phase. TRT process greatly affects the result of modification process. The compound treatment of TRT+ modification could increase the modification effects of Na or P element. According to the state and its change of Al-Si alloy melt, the test results were discussed.

Key words Al-Si alloys thermal rate treatment modification alloy melt

1 INTRODUCTION

Having good mechanical properties and perfect foundry technological properties, Al-Si based alloys have been widely applied to industrial productions. How to improve further the mechanical properties of the alloys has been the focal point of study, modification technique is the most practical method. We have designed a new kind of melting technique i. e. thermal rate treatment (TRT), which can greatly improve the properties and quality of some commercial alloys[1-3]. The authors designed TRT technique for Al-Si alloy and studied the effect of TRT process on modification process in order to explore a new way to improve further the mechanical properties of Al-Si alloy casting.

2 EXPERIMENTAL

Three kinds of Al-Si alloys were selected as test alloys, their chemical compositions were given in Table 1. The sodium-salt modifying agent used in the hypoeutectic and eutectic alloy was composed of 40% NaF, 40% NaCl and 20% KCl, the amount of the modifying agent used was equal to 2% of melted alloys. The phosphorus modifying agent used in the hypereutectic alloy was composed of 10% P_4 (red phosphorus) and 90% C_2Cl_6, the amount of the modifyihg agent used was equal to 0.35% of melted alloys; 0.4% C_2Cl_6 agent was used in a refining process. The sketch map showing TRT and conventional melting technique (CM) used in the paper is given in Fig. 1.

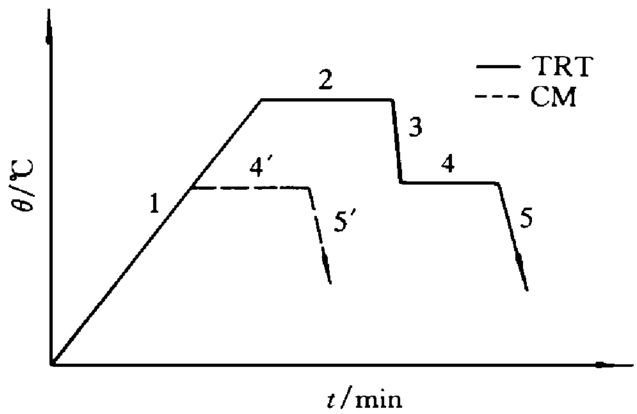

Fig. 1 Sketch map showing two melting techniques
1—melting, superheating;
2—setting;
3—chilling, stirring;
4—refining, setting;
4′-refining, modifying, setting;
5—pouring

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Table 1 Compositions of test alloys (%)

Alloy form	Si	Mg	Fe	Al
Hypoeutectic alloy	7~ 8	0.25~ 0.35	< 0.2	balance
Eutectic alloy	12~ 14	–	< 0.2	balance
Hypereutectic alloy	17~ 19	–	< 0.2	balance

3 RESULTS

3.1 Effect of TRT on impact toughness

Table 2 indicates that the impact toughness of hypoeutectic, eutecti and hypereutectic alloy treated with TRT technique increases 43%, 33% and, 20% respectively compared with non-modification(non-M) process; and that treated with modification (M) process increases 82%, 47% and 24%. So TRT process has obvious effect on the improvement of the alloy impact toughness, it also indicates that the effects of the modification and TRT lessen gradually with the increase of the Si content. Though the M result is better than TRT result, the difference between them is reduced with the increase of the Si content. The morphologies of alloys treated with different processes are showed in Fig. 2, it is found that TRT process makes the amount of white α phase

Table 2 Impact toughness of alloys treated with different processes

Alloy form	Process form	Impact toughness/ $J \cdot cm^{-2}$			
		1	2	3	Mean
Hypoeutectic alloy	Non-modifiction	23.19	23.10	24.18	23.49
	Modification	42.18	41.61	44.33	42.71
	TRT	34.71	32.69	33.40	33.60
Eutectic alloy	Non-modification	8.26	8.95	8.58	8.60
	Modification	12.70	13.26	12.06	12.67
	TRT	11.03	11.08	12.13	11.41
Hypereutectic alloy	Non-modification	5.58	5.70	5.24	5.51
	Modification	6.48	7.07	6.94	6.83
	TRT	5.83	7.66	6.90	6.61

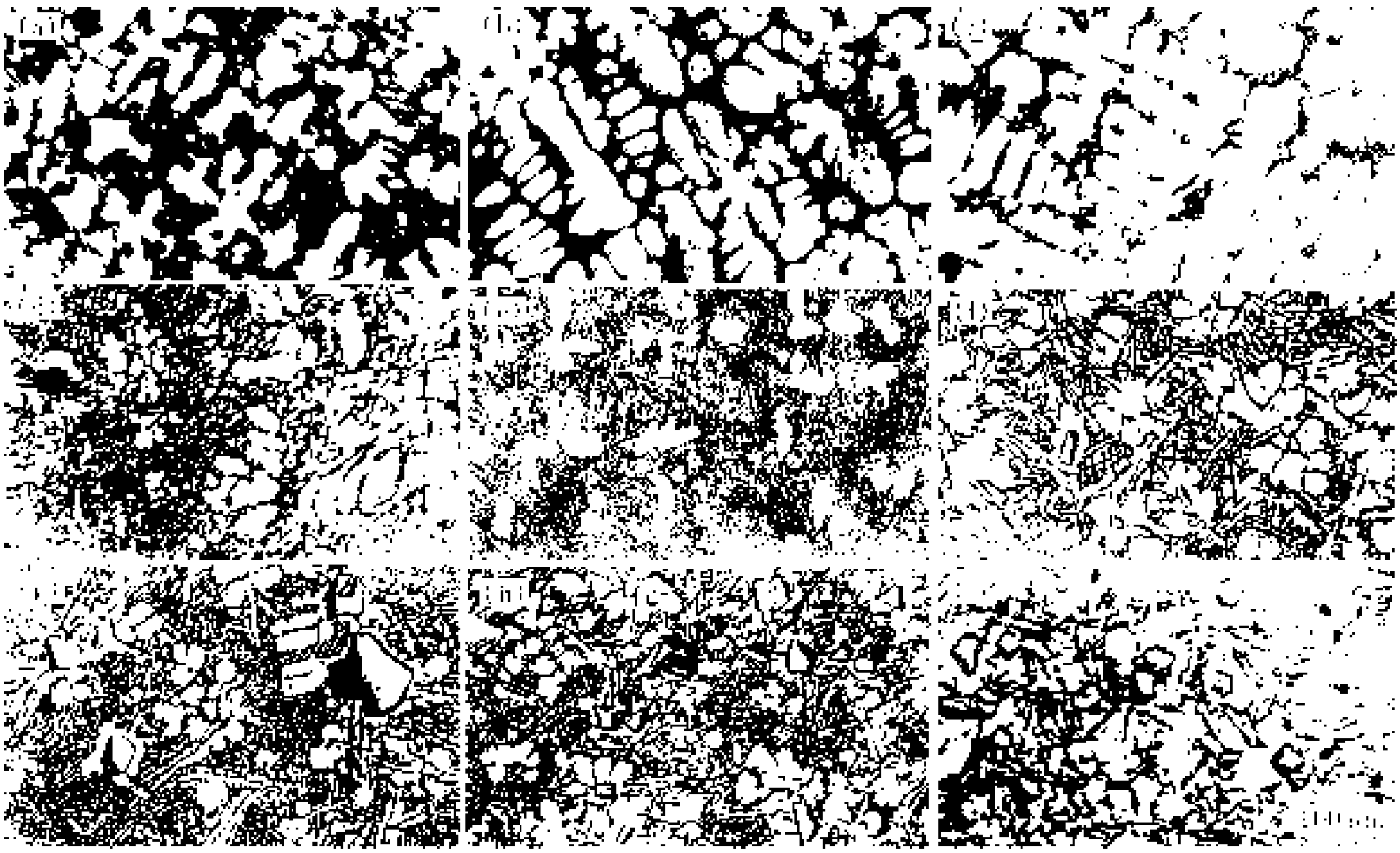

Fig. 2 Morphologies of alloys treated with different processes

(a) —hypoeutectic, non-M; (b) —hypoeutectic, M; (c) —hypoeutectic, TRT;
(d) —eutectic, non-M; (e) —eutectic, M; (f) —eutectic, TRT;
(g) —hypereutectic, non-M; (h) —hypereutectic, M; (i) —hypereutectic, TRT

increase and the alloy phase well distribute, the primary Si grain in the hypereutectic is refined. M process also refines the primary Si grain, changes the eutectic structure from thick flake-form to close-form, and the eutectic Si becomes fine grain-form. Therefore, effects of the M and TRT process on the alloy microstructure are different although they both improve the mechanical properties of the alloys, which means that mechanisms of the two processes are different.

3.2 Compound process tests

3.2.1 M+ TRT process

The sketch map of this test process is showed in Fig. 3. The impact toughness (a_k) of hypoeutectic and eutectic alloys that treated with different processes is showed in Table 3. The test results indicate that the a_k of the hypoeutectic and eutectic alloy treated with M process increases 91% and 56% respectively, then with TRT technique, the a_k decreases greatly. The a_k decreasing extent of the eutectic alloy is small than that of hypoeutectic alloy. Therefore, it is disadvantageous to carry on TRT process after M process.

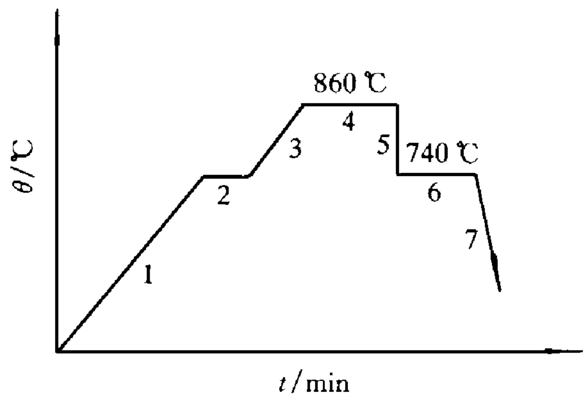

Fig. 3 Sketch map of M+ TRT process test
1—melting; 2—pouring non- M sample;
3—superheating; 4—modifying, setting,
pouring chill charge and M sample;
5—chilling; 6—refining, setting; 7—pouring

3.2.2 TRT+ M process

The sketch map of this test process is showed in Fig. 4. From Table 4, the a_k of the hypoeutectic, eutectic and hypereutectic alloy treated with TRT increases 45%, 34% and 22% respectively, then, with M process, the

Table 3 Result of M+ TRT process test

Alloy form	Process form	Impact toughness/ $J\cdot cm^{-2}$				
		1	2	3	4	Mean
Hypoeutectic alloy	Non-modification	20.6	21.7	21.2	22.0	21.4
	Modification	43.8	41.3	36.1	42.5	40.9
	M+ TRT	21.1	24.6	23.0	22.9	22.9
Eutectic alloy	Non-modification	7.9	8.4	8.5	8.7	8.4
	Modification	13.6	11.6	12.1	13.2	12.6
	M+ TRT	9.9	11.8	9.8	11.1	10.7

a_k increases 147%, 77% and 52% respectively compared with that of non-M process. The results here indicate again that TRT increases obviously the impact toughness of Al-Si alloys, especially for the hypoeutectic alloy. On the basis of TRT process, carrying on M process can improve further the mechanical properties. Compared with the results in Table 2, the result of TRT+ M process is better than that of sole modification process, which shows that carrying on TRT process before modifying is beneficial to the promotion of modification effect of Na and P element.

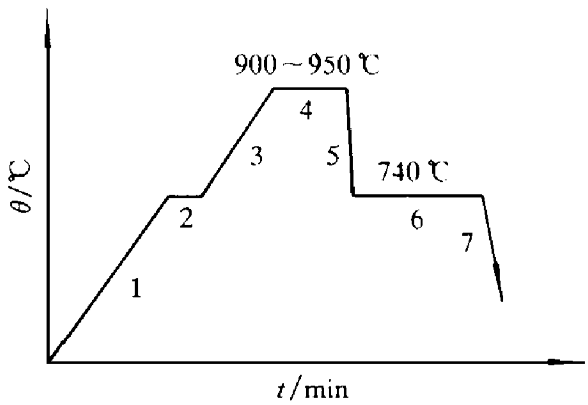

Fig. 4 Sketch map of TRT+ M process test
1—melting; 2—pouring non- M sample;
3—superheating; 4—setting, pouring
chill charge; 5—chilling;
6—refining; modifying, setting; 7—pouring

4 DISCUSSION

The test results above have demonstrated that the effects of the compound treatment do not reduplicate the effect of M and TRT technique, how to explain the results?

Table 4 Result of TRT+ M process test

Alloy form	Process form	Impact toughness/ J·cm^{-2}					
		1	2	3	4	Mean	Raising ratio/ %
Hypoeutectic	Non-modification	21.8	20.9	23.0	21.6	21.8	0
alloy	TRT	30.7	32.2	32.1	31.4	31.6	45.0
	TRT+ M	55.8	54.1	56.3	53.1	53.8	146.8
Eutectic	Non-modification	8.5	8.4	8.2	8.8	8.5	0
alloy	TRT	11.7	10.7	12.2	10.9	11.4	34.1
	TRT+ M	14.5	14.4	15.9	15.3	15.0	76.5
Hypereutectic	Non-modification	5.1	5.3	6.1	5.2	5.4	0
	TRT	6.8	6.4	6.3	7.1	6.6	22.2
	TRT+ M	7.8	9.0	7.5	8.5	8.2	52.1

An[4] thought that the metallic melt are composed of numerous clusters whose average size and travelling rate are related to temperature, therefore, the structure of Al-Si alloy melt is heterogeneous over a wide range of temperature, there would exist some clusters. The data in Table 5 shows that silicon has much higher melting point and sublimation heat, much smaller atomic radius and coefficient of linear expansion compared with aluminum, so the binding force among Si atoms is much stronger[5]. The binding energy among the atoms in liquid alloy is similar to that in solid alloy, so the binding ability among the atoms under high temperature state can be indicated with the aid of the dissociation energy of room temperature atomic bond. The dissociation energy of room temperature atomic bond existing probably in Al-Si alloy are showed in Table 6[6], it is evident that the binding of Si-Si atom bond is the largest, Al-Si the next. We come to the conclusion that there exist Si-rich clusters in the melts of eutectic or hypereutectic Al-Si alloy, these clusters would develop into the crystal nuclei for the primary or eutectic silicon. In hypoeutectic Al-Si alloy, the Si-Si atomic bonds are broken under the action of numerous Al-rich clusters owing to the lower Si amount. These Si-rich or Al-rich clusters would exist stably under their decomposing temperature, and cause the heterogeneity of the melts. Over the decomposing temperature, the clusters will decompose and disappear, the change of the melt microstructure appears. With Al-Si alloy melts, some heat effect peaks have been discovered on the test curves of the thermal analysis[1, 7], which demonstrates the change of Al-Si melt structure.

Table 5 Basic physical properties of Al and Si

Element	Melting point / ℃	Coefficient of linear expansion (20 ℃) / 10^{-6} ℃$^{-1}$	Atomic radius / Å	Sublimation heat / kJ·mol^{-1}
Al	660	22.4	1.428	75
Si	1410	6.95	1.08	90

Table 6 Dissociation energies of atomic bond in Al-Si alloy (25 ℃)

Atomic bond form	Al-Al	Al-Si	Si-Si
Dissoulation energy/ kJ·mol^{-1}	186.2	251	326.8

The high temperature superheating of the melt in TRT process decreases the amount and size of clusters, under the rapid cooling rate in the chill process, the homogenization of the melt remains to a large extent, the size of Si grain in the hypereutectic alloy is reduced, meanwhile, Si phase forming is controlled due to the reduction of Si-rich clusters, the crystallization and growth of the α-Al phase take precedence, so there are more α phases in the hypoeutectic and eutectic alloy treated with TRT.

According to the theory with the growth of Si crystal nuclei controlled[8], Na modifying element is adsorbed on the surface of the Si crystal unmelted in the melt or reacts upon the Si clusters in a film-form, the action of Si-rich clusters as Si crystal core is eliminated, which makes silicon not separate out early and limits the growth of Si crystal, in this way, the eutectic structure is refined. Phosphorus forms AlP compound particle which acts as heterogeneous Si crystal nucleus, so the primary Si is refined. There may be two reasons about the reduction of modification effect of Na in M+ TRT process: (1) the recession in the modification effect of Na at high temperature; (2) the Na film on the surface of Si crystal nuclei comes off owing to stirring violently in TRT process. In TRT+ M process, TRT improves the homogenization of the melt, that is, reduces the amount and size of the clusters, so the effective density of Na or P elements in the melt increases, the modifying effect are exerted further.

From the results above, it turns out that alloy melt state would affect the results of refinement or modification process, Unfortunately, this conclusion has not yet be noted generally, which is often the main cause why modification or refinement result is not stable in factory production. With TRT+ M technique, the modifying agent amount used can be reduce with the same mechanical properties of Al-Si alloys, in this way, some harmful effects caused by modifying agent, such as porosity or inclusion, can be avoided. Therefore, TRT + M technique provides us a new effective way to improve the properties and the quality of Al-Si alloy casting.

5 CONCLUSIONS

(1) TRT technique can obviously improve the impact toughness of Al-Si alloys, increase the amount of α phase increase, damage the completion of tree-form α phase and refine the primary Si phase in hypereutectic Al-Si alloy, however, has little effect on the eutectic structure of Al-Si alloys.

(2) Carrying on TRT process after modification process will deteriorate the modification effect of Na and P element.

(3) TRT + M compound treatment technique can promote the modification effect of Na and P element, which indicates that melt state has an important influence on the modfiication result.

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