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Influence of process parameters on thermal-rate treatment of ZA42 alloy^①

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[Abstract] Sand casting process and directional solidification technique combining thermal-rate treatment (TRT) were used. The influence of process parameters on TRT was investigated according to the values of impact toughness. At the same time, the mechanism of TRT was discussed. The results showed that TRT can improve the impact toughness of this alloy, while the hardness is basically constant. The time of heat preservation should not be more than 5 min. Different forms of cooling intensification additive have different effects among which the zinc ingot solidified in graphite mold is the best one that can improve impact toughness of samples by more than 80%. With increasing the cooling temperature, the value of $\alpha(\text{Al})$ crystal lattice constant increases. The element Sb has negative effect on TRT.

[Key words] Zr-Al alloy; thermal-rate treatment (TRT); parameters

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1 INTRODUCTION

In the inner of melt, there are many elementides or clusters and non-order regions. The higher the temperature is, the smaller the elementides and the larger the non-order regions are. But, the normal overheating temperature (100~200 °C above liquidus) is much lower than the temperature of non-order. In melt, there are many kinds of transformations of allotropies, which usually come true through the transition of some parameters in elementides. There are also many transitions among different non-order region structures. However all these transitions do not exit in the region with excessively high overheating temperature, and need certain time to finish. So the rapid solidification of melt at certain high temperature will restrain the transitions mentioned above and the microstructure at high temperature is kept down to room temperature^[1,2].

It has been proved by a great deal of investigations that there is hereditary relationship among solid (raw charging)-liquid (metal melt)-solid (metal product)^[1,3~6]. That is to say, the microstructure and properties depend on melt microstructure to a great extent.

As the new kind of die material and wearing resistant material, zinc-aluminum alloys have superiorities in several aspects such as mechanical properties, techniques and economical production, which enhances their competition. In recent years, this kind of alloys has been utilized in many fields. And the research work on this system has been developed by many researchers around the world^[7~11]. Many measurements have been adopted to improve the utilities of the alloys in this system. The liquid structure of an

alloy has an important influence on the quality and properties of castings^[12,13]. The intention of the technique of TRT (thermal-rate treatment) is to control the quality and properties of castings utilizing the heredity of microstructure. In this paper, sand casting process and directional solidification technique are used combining TRT. ZA42 zinc alloy is chosen and the influence of process parameters on the TRT is investigated according to the values of impact toughness. The influence of the thermal-rate treatment and its mechanism are discussed with the help of TEM, etc.

2 EXPERIMENTAL

The purities of the materials used in the experiment were Al-99.7%, Zn-99.9%, and Cu-99.9% respectively, in which copper was in the form of intermetallic compound Al-50% Cu (mole fraction). The alloy was melted in the graphite melting crucible, which was put into the resistance furnace. The samples used were prepared by casting technique in which the condition was similar to the one of practical production. The chemical composition of this alloy is listed in Table 1. The samples for impact toughness test were cuboids whose gauge is 10 mm × 10 mm × 50 mm.

The influence of the time of heat preservation on TRT was studied by testing the sample impact toughness of the same group treated with different heat preservation durations.

A series of tests were held adopting different forms of cooling intensification additives in order to examine the influence of additive on the TRT. And in the further study, the mechanism of the effects of

cooling temperature on the TRT was discussed superficially.

In order to investigate the function of the element Sb to TRT, a certain amount of Sb was added into ZA42 alloy named in this paper ZA42b (shown in Table 1), the alloy without Sb was named ZA42a for comparison.

For further study, the analysis of TEM metallographical phase was done.

Fig. 1 is the sketch of TRT process, where curve 1 describes the normal process that provides the necessary data for comparison. Curve 2 represents the TRT process. The related parameters are set out in Table 2.

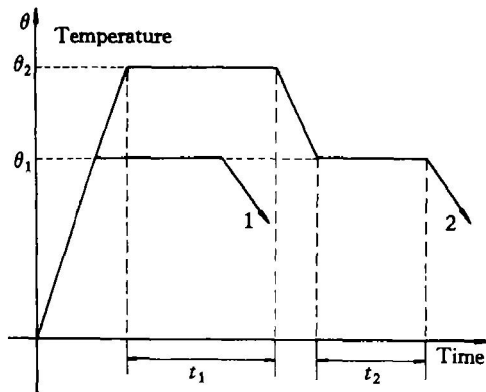


Fig. 1 Sketch of TRT process
(1) —Normal process; (2) —TRT process.

From the Zr-Al binary phase diagram (shown in Fig. 2), it can be seen that with increasing aluminum content, the distance between the liquidus and the solidus enlarges. The alloys tend to volumetric solidification resulting in the yielding of defects such as shrinkage, segregation. In order to eliminate or lessen the disadvantageous factors of this aspect, a chill (seen in Fig. 3) was used to create conditions for directional solidification, when the pure raw materials were melted.

3 RESULTS

3.1 Low temperature heat preservation tests

The focus is on the stability of TRT effects, that is to say how long the heat preservation does TRT dot best, and how about the wither speed, a group of tests with different heat preservation durations were held. The experiments were done as follows: when the alloy melted, cast for the first time at 640 °C and got the first group samples. At the same time 1/4~1/3 amount of the rest was poured into a metal mold

as additive (cooling in air). The melt in crucible was heated up to 810 °C when the cooling intensification additive was added. The 2nd, 3rd and 4th groups of samples were gotten after the molten alloy heat preserved for 5, 45 and 105 min, respectively. The impact toughness examination and HB test were held for the four group samples. And the results were shown in Table 3.

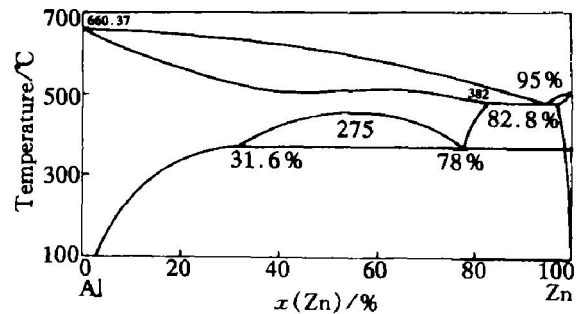


Fig. 2 Zr-Al binary diagram

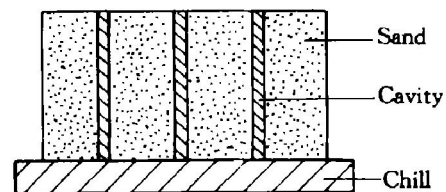


Fig. 3 Sketch of directional solidification

The time in Table 3 means the length of heat preservation time. Namely, t_2 was equal to 5, 45 and 105 min respectively.

From the data in Table 3, the results of TRT can be seen. And the best result should be controlled in certain period of time.

For the value of the impact toughness α_k went down, the degree of effect decayed with the time t lapsing. The ratio of α_k increment came to a head of 46.5% when heat preservation time of the melt after high temperature of 810 °C was 5 min. However, the ratio of α_k increment touched the bottom of only 9.8% when heat preservation time of the melt was 105 min. The reason for this phenomenon is that the changes of melt inner microstructure have a certain degree of reversibility. The cooling process of melt is also the process during which the microstructure of liquid metal reconverts to that of lower temperature of 640 °C. Therefore there is a tendency for the lower temperature melt to separate out a certain amount of primary phase, recombine radicles or clusters and the composition is uneven.

Table 1 Chemical compositions of Zr-Al alloys(%)

Alloy	Al	Cu	Mg	Sb	Fe	Zn
ZA42a	41~ 43	2.0~ 2.5	0.03~ 0.04	0	< 0.01	Balance
ZA42b	41~ 43	2.0~ 2.5	0.03~ 0.04	0.5	< 0.01	Balance

Table 2 Process parameters in TRT process

Parameter	Value
θ_1	640 °C
θ_2	810 °C
t_1	10 min
t_2	5~ 105 min

Table 3 Examination results of different heat preservation durations

Technique	HB	$\alpha_k /$ (J·cm ⁻²)	Amplification of $\alpha_k / \%$
Normal melting	112	27.22	
TRT, 5 min	106	39.88	46.5
TRT, 45 min	108	33.53	23.2
TRT, 105 min	104	29.88	9.8

It suggests that pouring process should be carried through when the melt is mixed up and set for 5 min, which is effective to avoid the decay of TRT. In addition, the values of HB in Table 4 also have a tendency of decreasing, but at the same time it can be seen that the ratio is very low. It means that the change of plasticity plays an important role in the whole process.

3.2 Different forms of cooling intensification additive

In this part of experiment, different forms of cooling intensification additive were adopted in order to examine the influence of parent materials on TRT.

In Table 4, A1 is the Zn ingot cooled in graphite mold, A2 cooled in metal mold, A3 cooled in sand mold, A4 cooled slowly in furnace respectively. It is very clear that when the form is A1, the value of impact toughness α_k is the maximum one. When the form is A4, however, the value α_k is the minimum one. That is to say, the more rapid the cooling rate of cooling intensification additive acquired in different molds is, the more effective the function is.

Table 4 Impact toughness results of different forms of cooling intensification

Form	$\alpha_k /$ (J·cm ⁻²)	Ratio of α_k increment/ %
Normal melting	25.06	
A1	45.17	80.3
A2	37.17	51.7
A3	28.49	13.7
A4	28.03	11.9

The other conclusion can be drawn that under the circumstances of the cooling rate almost being the same, the original microstructure of material plays an important role and provides the seeds of crystallization in the process of rapid solidification. It just proves the

usage of heredity.

The reason of using metal Zn as cooling intensifier in the test is that Zn has lower melting point and specific heat capacity, which means that it is easy to control the process.

3.3 Influence of Sb on TRT

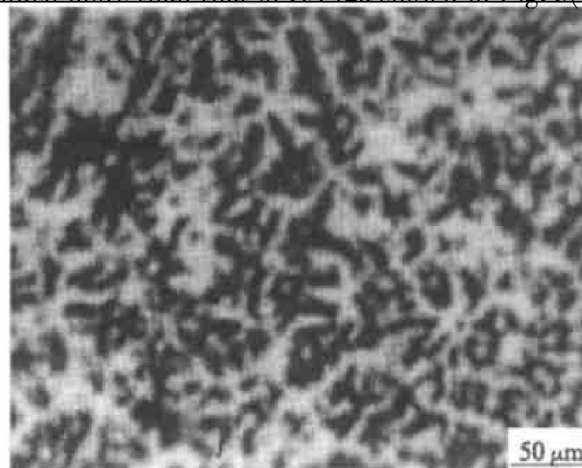
Element Sb can improve the dimensional stability of Zn based alloys, lessen the amount of defects, and enhance wearing resistance and load-bearing capacity.

A series of impact toughness values are given in Table 5. The chemical composition of ZA42a and ZA42b is listed in Table 1. ZA42b (1) is the one without TRT; ZA42b (2) is the other one with TRT. The ratio of impact toughness increment of ZA42b (1) to ZA42a is 26.46%, which means that the element Sb is able to improve the mechanical properties of ZA42 alloy. However, after TRT, the impact toughness decrease by 25.59%, comparing with the one without TRT, and 5.91% with ZA42a, respectively. That is to say, the TRT weakens the function of element Sb.

Table 5 Influence of Sb on TRT

Alloy and treatment	$\alpha_k /$ (J·cm ⁻²)	Ratio of α_k increment/ %
ZA42a	25.06	
ZA42b (1)	31.69	26.46
ZA42b (2)	23.58	- 5.91

Fig. 4 shows the microstructure of ZA42 containing Sb without TRT. The content of white phase is much more than that of ZA42a shown in Fig. 5(a).

**Fig. 4** Microstructure of ZA42b

It is believed that when element Sb was added into ZA42 alloy, two kinds of compounds Sb-Al-Zn and AlSb distributing as particles along the boundaries among different crystals to change matrix structure, which provides the wearing resistant particles and enhances wearing resistance of this stuff.

4 DISCUSSION

Fig. 5 shows the microstructures of ZA42 alloys of different states, in which (a) is one of normal microstructure without TRT, and (b) is one with certain TRT. The continuous dendrites (white phase) were broken up distributed uniformly. In addition, as the transition phase, the content of gray phase increased.

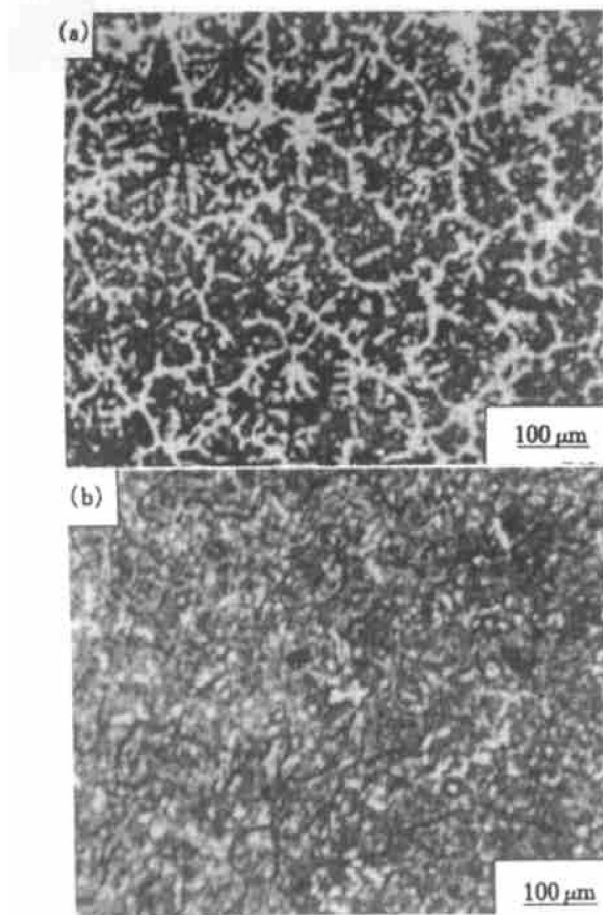


Fig. 5 Microstructures of ZA42a
(a) —Without TRT; (b) —TRT

Maybe the reason why TRT can enhance the properties of this alloy is that superheating exerts an important influence upon nucleation whether in normal course of production or as a preliminary treatment. The mechanism of refining by superheat may be explained as that the relatively large solid solution includes particles of nucleating compounds and they precipitate more finely and in crystallographically favorable direction. Thus the entire state of thermal of the molten can affect the microstructure after solidifying.

The association of rapid cooling with fine grain size arises from the influence of undercooling at the comparative rates of nucleation and growth. The influence of very high cooling rates in producing fine structures also offers possibilities for the future development of high strength casting alloys.

As viewed from liquid structure, there are many Al-rich, Zr-rich and other clusters existing in the melt. And these clusters are not stable. That is to

say, these clusters change continuously. It can be thought that there is composition fluctuation. The clusters provided the seeds of crystallization in the process of rapid solidification. In higher temperature melt, there are less clusters and the composition fluctuation is weaker than that in the lower temperature melt. And under the condition of longer heat preservation time, the Al-rich clusters, Zr-rich clusters and other clusters have more time to grow. So there will be more crystal nuclei and the microstructure will be different from that of high temperature melt where there are less big grains. So the TRT effects will decrease.

From the point of heredity, the larger the rapid cooling rate is, the more the features can be saved. So the forms of cooling intensification have an important influence on TRT, which can provide the seeds for crystallization. Different nature of cooling intensification additive results in different influence of rapid solidification on the microstructures of alloys.

It is the result gotten from the two aspects mentioned above when using cooling intensification additive to fulfill TRT process.

The diffraction design (shown in Fig. 6) of α (Al) solid solution in different cases was gauged. According to the condition of experiments, there is an experimental formula:

$$d = \frac{\lambda \cdot L}{R} = \frac{0.027 \times 780}{R} = \frac{21.6}{R}$$

where R is the distance between spots; d is the space between the abut layers; L is the length of camera; λ is the wavelength of incidence electrons.

The results suggest that the lattice constant of α (Al) solid solution is larger in alloy treated by TRT (b) than that in the alloy without TRT (a).

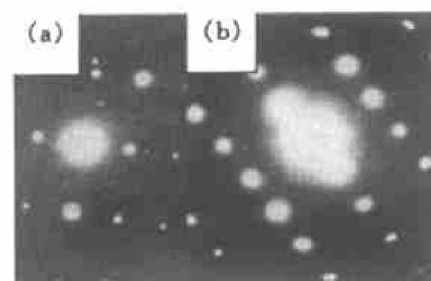


Fig. 6 Diffraction design of α (Al)
(a) —Without TRT; (b) —TRT

The increase of mixing degree of elements in high temperature melt provides the suitable conditions to the possibility of forming crystal lattice positive distortion, which can be explained more clearly using the relative theories of thermodynamics and kinetics. Because of the increase of atomic energy, rapid solidification of melt urges the increase of vacancy thickness to be kept in crystal. It forces the α (Al) to do some positive distortion, which makes the lattice constant be larger. In some cases, the change mentioned

above provides the favorable influence on the mechanical properties and quality of castings^[7, 13].

The addition of antimony can form certain compounds that have the effect on grain refining. So the mechanical properties are improved^[14]. However, when the melt was treated by overheating, the compound Sb-Al-Zn decompounded and formed brittle compound AlSb, which distributes along the crystal boundaries. AlSb decreases impact toughness. Under the conditions above, TRT is unwanted.

The element Sb works in two ways. One is that when the temperature of the ZA42 melt is much higher, Sb has negative effect on the microstructure fining and composition uniformity of the ZA42. The other is that there are some Sb-rich phases or AlSb and other compounds which destroy the original microstructure.

5 CONCLUSIONS

1) TRT can enhance the impact toughness of the alloy, while the hardness keeps basically constant;

2) When the temperature decreased to the lower one, the length of heat preservation time should be not more than 5 min;

3) The effects of TRT decrease with increasing heat preservation time;

4) The forms of cooling intensification additive have notable influence to TRT. As the best kind of cooling intensification additive, the ingot cooled in the graphite mold can increase impact toughness by more than 80%;

5) Sb is able to enhance the properties of ZA42 alloy, but its function is in contradiction with TRT.

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