

Effects of cooling rate on solidification behavior of dilute Al-Sc and Al-Sc-Zr solid solution^①

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Abstract: Six alloys with different compositions of Al-0.1% Sc, Al-0.3% Sc, Al-0.3% Zr, Al-0.1% Sc-0.1% Zr, Al-0.3% Sc-0.1% Zr and Al-0.3% Sc-0.3% Zr were prepared by casting in a wedge shaped copper mould. The hardness test, microstructure observation, and DSC thermal analysis were applied to fully investigate the solidification behavior of the wedge tip (whose cooling rate is 1 000 K/s) and the top surface (cooling rate 100 K/s) of each casting. The results show that the cast structures in the hypoeutectic region of Al-Sc alloys are slightly affected by cooling rates during the solidification. In the case of hypereutectic alloy of Al-0.3% Sc-0.3% Zr, the cast grains were remarkably refined under the condition of a 100 K/s cooling rate, however, under a 1 000 K/s cooling rate condition, solute atoms contribute nothing to the grain refinement, due to the eutectic concentration becomes higher. The hardness can be improved to a greater degree by Sc single addition, compared to single Zr addition, but it can be improved even greater when Sc added together with Zr. It is sensitive to cooling rate, the higher the cooling rate, the greater the hardness. By combining the results of TEM examination and DSC analysis, it can be seen that a supersaturated Al solid solution forms during the solidification, and the solubility of Sc in Al solution can be improved by increasing the cooling rate.

Key words: Al-Sc; Al-Sc-Zr; solidification; cooling rate; solid solubility

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1 INTRODUCTION

The various properties of Al alloys can be improved in many ways by the addition of Sc. The main benefits of Sc addition can be summarized as follows: (a) the Al-Sc solid solution decomposes to form a L1₂ type Al₃Sc phase matching with the matrix, which can produce a precipitation hardening^[1-3]; (b) the fine dispersed Al₃Sc particles can tightly pin up the grain boundaries and the dislocations, and also inhibit the recrystallization, so the alloy can be deforming strengthened (defects being introduced)^[3,4]; (c) cast grains can be well refined^[5]; (d) weldability of Al alloys can be improved^[6-8]. All these benefits are related to the solubility of Sc in Al alloys.

However, the binary Al-Sc phase diagram^[9] reveals that under equilibrium condition, the limit solubility of Sc in Al is low (0.32%). Therefore, how to improve the solubility of Sc in Al is critical to make the Sc act efficiently. In addition, it's a tendency to have partial Zr taken place by Sc in Al alloys, because Zr can substantially incorporate into Al₃Sc phase (up

to 50%) to form a Al₃(Sc_{1-x}Zr_x) phase^[10, 11] (whose structure type and lattice parameter are close to Al₃Sc phase). Therefore, it is very important to further investigate the solution behavior and the effect factors of Sc and Zr in Al alloys. The effect of cooling rates on the solidification behavior of Sc and Zr in high pure Al is mainly focused in this paper.

2 EXPERIMENTAL

Different cooling rates during solidification of Al alloys are gained through a wedge shaped copper mould, whose sizes are shown in Fig. 1. When the Al alloy melt solidifies in this mould, the cooling rate corresponding to the wedge tip is about 1 000 K/s, and the top surface, lower than 100 K/s.

The wedge ingots of six different compositions studied in this experiment were prepared by using high pure Al (99.99%), Al-3.2% Sc and Al-3.0% Zr master alloys. A crucible furnace was used for melting. The melting temperature was about 780 °C, and the casting temperature was 720 - 750 °C.

Samples for hardness test, OM observation,

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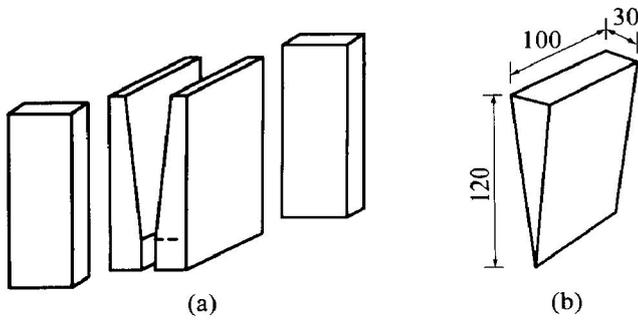


Fig. 1 Schematic diagram of wedge-shaped copper mould and casting dimensions (mm)

TEM examination and DSC analysis were taken from a 20 mm distance to the wedge tip and the top surface of the wedge ingots. Foils for TEM examination were prepared in double-spray electropolishing method. The solution was 30% nitric acid and 70% methanol. The electrolytic voltage was about 20 V, the current was 80–100 mA, and the temperature was controlled at $-30\text{ }^{\circ}\text{C}$. Foils observation was carried out in a Tecnai 20 electron microscope, operated at 200 kV. In order to compare the solid solubility of Sc with Zr in Al solution qualitatively under different cooling rates, the DSC analyses of the Al-0.3% Sc, Al-0.3% Zr and Al-0.3% Sc-0.3% Zr alloys were undertaken in a NETSCH thermal analyzer. The disc samples, 4.5 mm in diameter, 1 mm in thickness, were also cut from the two sections of the wedge ingots. In order to eliminate the influence of the matrix, the DSC curve of a high pure Al under the identical condition as the background was subtracted from the alloy DSC curves.

3 RESULTS AND DISCUSSION

3.1 Hardness testing

The hardness of each cast ingot, corresponding to the most extreme cooling rates on the tip and the top surface, respectively, is demonstrated in Fig. 2, under the conditions above. The single addition of Sc contributes more to the alloy hardness, compared to Zr. For joint addition of them, the hardness of each alloy is sensitive to the cooling rate. With increasing cooling rate, the hardness improves, too, which suggests that the solubility of Sc and Zr in Al solution can be increased by increasing the cooling rate during the solidification of the alloys.

3.2 Microstructure observation

The cast structures of six different compositions associated with different cooling rates are shown in Fig. 3 and Fig. 4. It can be seen that, in general, the increase of cooling rates is in favor of the refinement

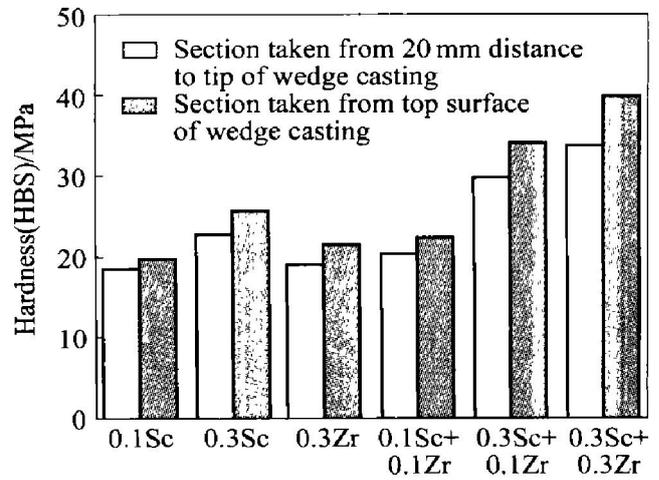


Fig. 2 Hardness tested at different cooling rate sections of wedge castings

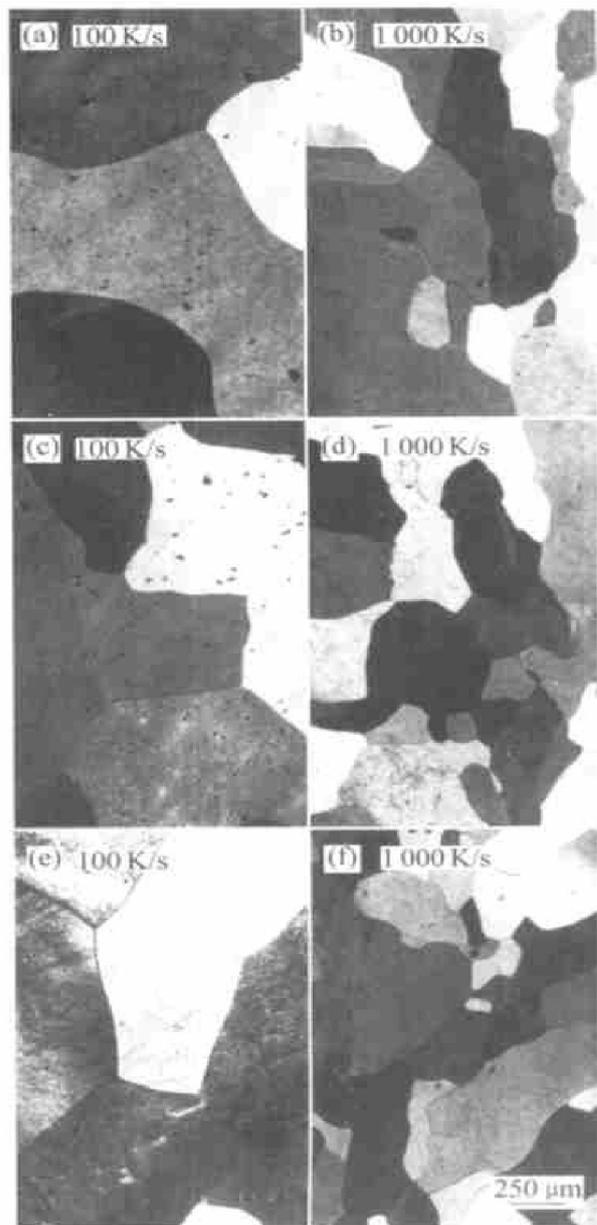


Fig. 3 Solidification microstructures of different sections taken from wedge casting (a) and (b) —Al-0.1% Sc; (c) and (d) —Al-0.3% Sc; (e) and (f) —Al-0.3% Zr

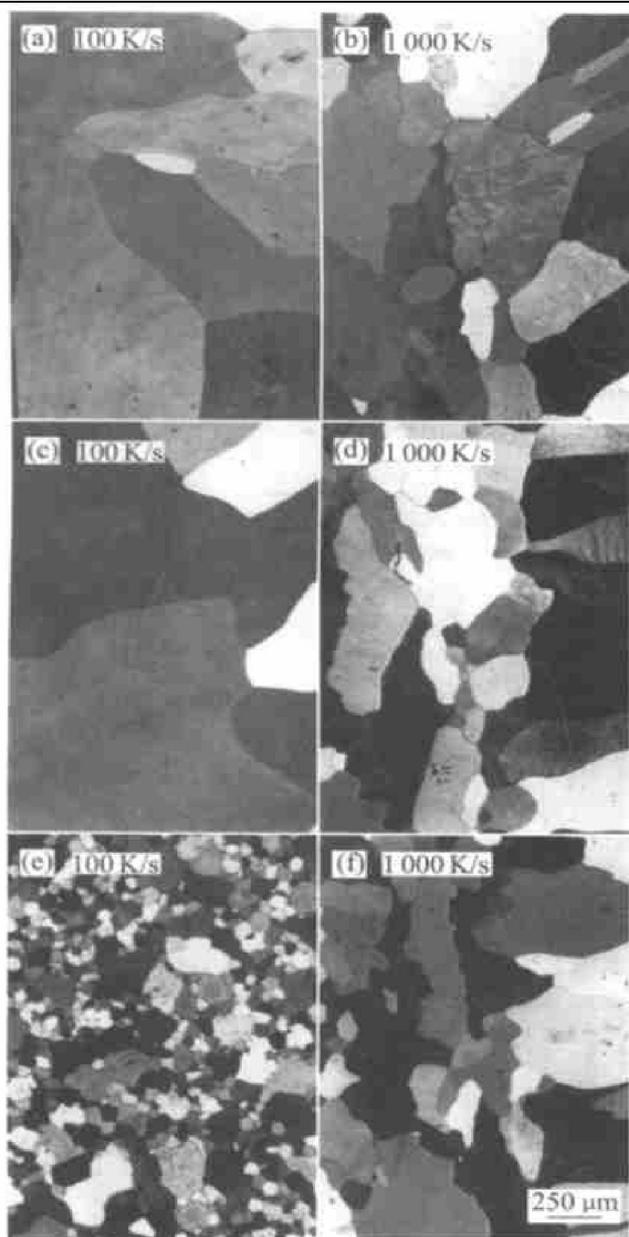


Fig. 4 Solidification microstructures of different sections taken from wedge casting

- (a) and (b) —Al-0.1%Sc-0.1%Zr;
 (c) and (d) —Al-0.3%Sc-0.1%Zr;
 (e) and (f) —Al-0.3%Sc-0.3%Zr

of cast grains (except Al-0.3%Sc-0.3%Zr alloy), shown in Figs. 3(a)–(f) and Figs. 4(a)–(d). However, the amount of Sc and Zr addition does not have great effect on the grain refinement. This can be interpreted that the compositions of the alloys being in the hypoeutectic region, a supersaturated solid solution forms due to a high cooling rate, which results in the alloying elements contributing nothing to the grain refinement. Although the cooling rate corresponding to the wedge tip is high, columnar grains still can be observed clearly near the mould wall.

The composition of the Al-0.3%Sc-0.3%Zr alloy is in the hypereutectic region of equilibrium state. At the casting top surface, primary Al_3Sc particles

form before eutectic reaction due to the fact that a low cooling rate during the solidification could provide a heterogeneous nucleation site, which refines the cast grains of the alloys, as shown in Fig. 4(e). But in the case of the casting tip, due to a high cooling rate, the eutectic point of the Al-Sc alloy shifts to the right (amount of Sc containing increased), which leads the alloy to being in the hypoeutectic region, thus the alloying elements have no influence on the grain refinement, as shown in Fig. 4(f). Therefore, the cast structures of Al-Sc alloy system depend on the cooling rate very much. A supersaturated solid solution containing substantial Sc can be obtained by increasing the cooling rate.

3.3 TEM examination

The TEM examination results of typical cast microstructure under different cooling rates are shown in Fig. 5. Compound phase can't be seen neither at the grain boundaries nor within the grains of the wedge casting tip of Al-0.3%Sc alloy. This demonstrates that the added Sc has dissolved into Al crystal lattice and formed a supersaturated solid solution. However, a small amount of eutectic structure of $\alpha\text{Al} + \text{Al}_3\text{Sc}$ can be found at the boundaries of the casting top (Fig. 5(b)), which indicates that the solute element Sc did not fully dissolve into the Al matrix due to the low cooling rate. As for the tip of Al-0.3%Sc-0.3%Zr cast ingot, coarse compound phase can't be observed within the crystals, but at the boundaries, it can be seen occasionally (Fig. 5(c)). On the top, corresponding to a lower cooling rate, eutectic structures formed at the grain boundaries are apparently increased, as shown in Fig. 5(d).

From the above observation results, the solubility of Sc in Al do can be enhanced by increasing the cooling rate, but there exists a limit. In this experiment, when the cooling rate is close to 1 000 K/s (wedge cast tip), the total amount of Sc and Zr addition being up to 0.6%, Sc and Zr can not be fully dissolved into the Al solid solution.

3.4 DSC analysis

The lattice parameter of the αAl solid solution of Al alloy system is strongly affected by the H atom, so it is not very accurate to determine the solubility of Sc and Zr in the αAl solid solution just by the way of testing the lattice parameter. Therefore, DSC analysis is applied to compare the solubility of Sc with Zr qualitatively, through measuring the exothermic peak area during the process of the precipitates' decomposing when the αAl solid solution was heated.

3.4.1 Al-0.3%Sc and Al-0.3%Zr alloys

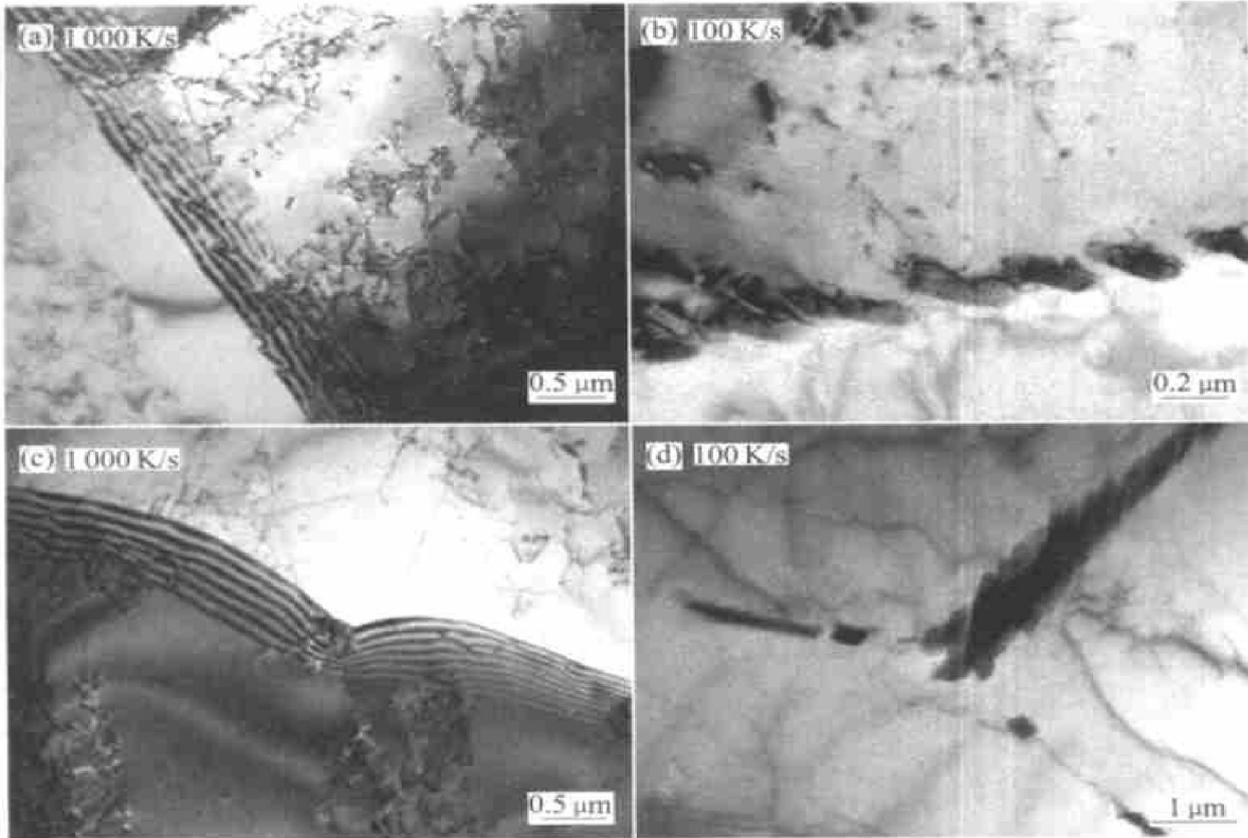


Fig. 5 Solidification microstructures at grain boundaries of different sections taken from wedge castings (a) and (b) —Al-0.3%Sc; (c) and (d) —Al-0.3%Sc-0.3%Zr

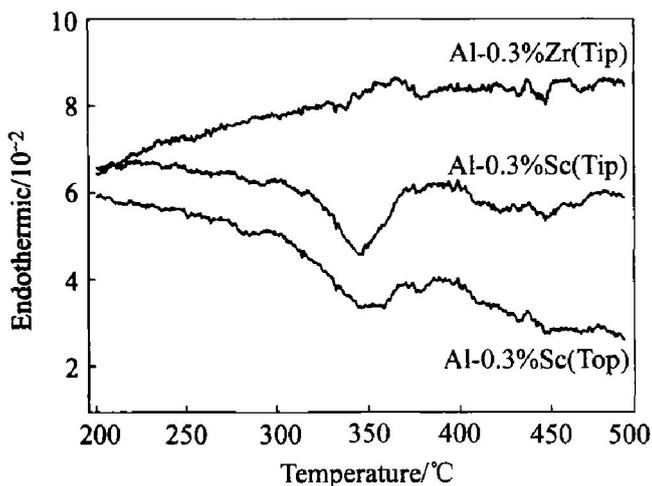


Fig. 6 DSC thermograms of different cooling rate sections of Al-0.3%Sc and Al-0.3%Zr alloys

The DSC results of each sample taken from the wedge tip, as well as the top, of Al-0.3%Sc and Al-0.3%Zr alloys, respectively, are shown in Fig. 6, after removing the influence of the background. Obviously, there is a very small exothermic peak near 375 °C in the tip sample of Al-0.3%Zr alloy (Fig. 6, Al-0.3%Zr (Tip) curve), and the peak corresponds to the sub-stable Al_3Zr phase (LI_2 type) precipitated from the solid solution. But in the case of the sample taken from the top, there is no appearance of the exothermic peak (not demonstrated), which suggests that the solubility of Zr in Al is very low, and it can't

be slightly increased even by increasing the cooling rate within the permission range in this work. As for the appearance of fine grains above 425 °C, it can possibly be explained that the sub-stable Al_3Zr phase decomposes (corresponding to the endothermic peak) and then forms the equilibrium Al_3Zr phase (square structure).

The other two curves in Fig. 6 show that the exothermic peak of the Al-0.3%Sc alloy is much bigger than that of the Al-0.3%Zr alloy, which suggests that the solubility of Sc is greater than that of Zr, and improves with increasing cooling rate (Tip). The exothermic peak of the Al-0.3%Sc alloy occurs at about 325 °C, corresponding to the sub-stable equilibrium Al_3Sc phase (LI_2 type) which precipitates from the α -Al solid solution. This precipitation system has no transition phases, and the stable Al_3Sc phase forms directly. The starting temperature of the Al_3Sc precipitation is at about 245 °C when a usual mar-controlled aging treatment was carried out. This temperature is different with the DTA result to some extent. This is because the Al_3Sc phase has a relatively long gestation period to precipitate, and it just takes 8 min for the temperature to increase from 245 °C to 325 °C when the ratio is 10 °C/min in DTA test. As a result, when it increases to the precipitation starting temperature, the Al_3Sc phase does not have enough time to precipitate before the temperature arrives at a high one, which produces a departure in the test results.

3.4.2 Al-0.3%Sc-0.3%Zr alloy

The DSC test results of samples taken from the wedge casting tip and top of the Al-0.3%Sc-0.3%Zr alloy are shown in Fig. 7. It can be seen that the solubility of the solute of the Al-0.3%Sc-0.3%Zr alloy is also related to the cooling rate, the higher the cooling rate, the bigger the exothermic peak space, and the greater the solid solubility accordingly. The position of the exothermic peak of the cast alloy is the same as that containing Sc only, which reveals that the exfoliation precipitation is still Al_3Sc , and the Zr addition does not modify the solidification behavior of the exfoliation precipitation of the Al-Sc alloys.

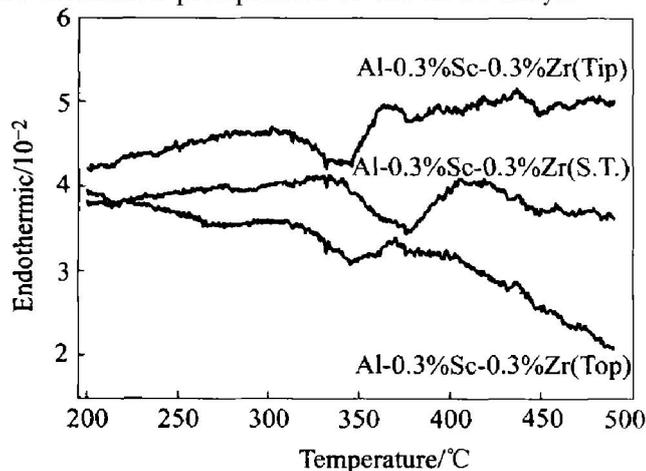


Fig. 7 DSC thermograms of different cooling rate sections of Al-0.3%Sc-0.3%Zr alloy

The curve of the Al-0.3%Sc-0.3%Zr alloy (S. T.) shown in Fig. 7 is obtained by testing the solid solution treated sample. The specimens were heated up to 635 °C and kept for 2 h, then quenched in cold water. The purpose is to investigate whether the solubility of Sc and Zr in Al solution can be improved by the solution treatment. Seen from Fig. 7, the area of the exothermic peak of the solid solution treated sample is bigger than that of the cast sample which corresponds to a low cooling rate, but is close to that corresponding to a high cooling rate. These suggest that the solution treatment can improve the solid solubility of Sc and Zr in Al to some degree, but it does not have obvious influence on those alloys corresponding to a high cooling rate.

For the Al-0.3%Sc-0.3%Zr alloy being solution treated, its exothermic peak of the precipitates lag behind that of the cast alloys, occurring at about 375 °C. The reasons that the solution treatment makes the gestation period of the precipitation of the Al_3Sc phase longer or that the $Al_3(Sc, Zr)$ phase is precipitated need further investigation.

4 CONCLUSIONS

1) The hardness of the alloys can be improved to a much greater degree by the single addition of Sc, compared to Zr. For joint addition, the hardness is

sensitive to the cooling rate, and increases with the elevating of the cooling rate.

2) Casting grains can be remarkably refined by Sc addition to the hypereutectic Al-0.3%Sc-0.3%Zr alloy, when the cooling rate is 100 K/s, but for the 1 000 K/s cooling rate, Sc addition contributes nothing to the grain-refinement. Furthermore, compounds on crystal boundaries decrease significantly, so a super-saturated solid solution containing Sc can be obtained by increasing the cooling rate.

3) DSC analysis results show that it is an efficient way to improve the solid solubility of Sc in Al solution by increasing the cooling rate, but solution treatment has little effect on the improvement of the solid solubility of Sc and Zr in Al.

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