

# Effects of Cooling Rate and Supercooling Degree on Solidified Structures of Al-Mn, Al-Cr and Al-Zr Alloys in Rapid Solidification\*

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Effects of supercooling and cooling rate on the solidified structures of Al-Mn, Al-Cr and Al-Zr alloys, which had a strong tendency to form metastable solid solution by rapid cooling of the molten alloys, were investigated by means of thermal analysis and microscopic observation. The results obtained were as follows :

(1) The square of the degree of supercooling was proportional to the cooling rate on the solidification of the alloys having a solute concentration up to the maximum solid solubility limit at equilibrium ( $C_e$ ). At solute concentrations higher than  $C_e$ , this relation was satisfied under the conditions that the primary crystals were a super-saturated solid solution.

(2) The minimum cooling rate to form the super-saturated solid solutions containing more solute atoms than  $C_e$  was 115, 175 and 190°C/sec for Al-Mn, Al-Cr and Al-Zr respectively.

(3) Metastable phase diagrams were proposed under varying conditions of composition, temperature and cooling rate in the Al-Mn, Al-Cr and Al-Zr systems.

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## I. Introduction

The degree of supercooling and the cooling rate on the occasion of solidification of molten alloys are powerful factors to influence the solidified structures during the process of founding. The degree of supercooling depends on kinds and numbers of the nucleation catalysts such as the inside surface of the vessel and small particles suspended in the molten metals as insoluble impurities and oxides or formed by superheating and other treatments<sup>(1)</sup> of the liquid. On the other hand, the cooling rate is regarded as one of the other factors<sup>(2)</sup> controlled the degree of supercooling, but it has not as yet been satisfactorily explained.

In the present study, it was assumed as the condition of solidification that heterogeneous nucleation did not occur in suspending materials in the molten metals but occurred on the mould surface because of a rapid cooling of the molten metals. In the case of such solidification, the effects of the degree of supercooling and the cooling rate on the solidified structures of various alloying contents were investigated by an improved technique of thermal analysis and by observations of microstructures of Al-Mn, Al-Cr and Al-Zr alloys which had a strong tendency<sup>(3)~(5)</sup> to solidify to super-saturated solid solution structures by rapid cooling of the molten alloys.

## II. Experimental Procedure

Metals and alloys used as test pieces were commercial purity aluminium (99.8%) and Al-17.1% Mn, Al-9.96

% Cr and Al-5.12% Zr master alloys, the compositions of specimens being 1, 2, 3, 4, and 5% Mn, 0.5, 1, 1.5, 2, and 3% Cr and 0.5, 1, and 1.5% Zr respectively.

These molten alloys were made into ingots weighing 300~350 g, 35~40 g of which was melted at 840°C in the Al-Mn and Al-Cr systems and at 50°C above the liquidus temperature in the Al-Zr system and then was cast into a wedge-shaped copper mould cooled by water. The cooling process was measured by the thermo-couples set in the mould. The shape of specimens obtained was 18 mm in width, 100 mm in length and 7° in wedge angle.

The apparatus for thermal analysis was, as shown in Fig. 1, that an electric furnace in which a crucible having a hole at the bottom was set was fixed at the upper part of the apparatus, and a copper mould in which a wedge-shaped specimen was expected to be formed was fixed at the lower part of it. The hot junction of thermo-couples was set at 5 points at a same interval on the center line of the wedge-shaped cave in the mould, and the thermo-couple set in the mould was pre-heated at 800°~850°C under a low electric current. A trigger was placed between the crucible and the mould, and when the molten alloy fallen down from the hole at the bottom of the crucible made a short circuit with the trigger, the relay was set in motion and the value of the thermo-electromotive force indicating the temperature of the pre-heated thermo-couple was changed over to that of the temperature of the molten alloy fallen into the mould and then the solidification process was recorded by an X-Y recorder or an oscilloscope without delay<sup>(6)</sup>.

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(2) V. Kondic and D. Shutt : J. Inst. Metals, **78** (1950~51), 105; J. A. E. Bell and W. C. Weingard : *ibid.*, **94** (1966), 226.

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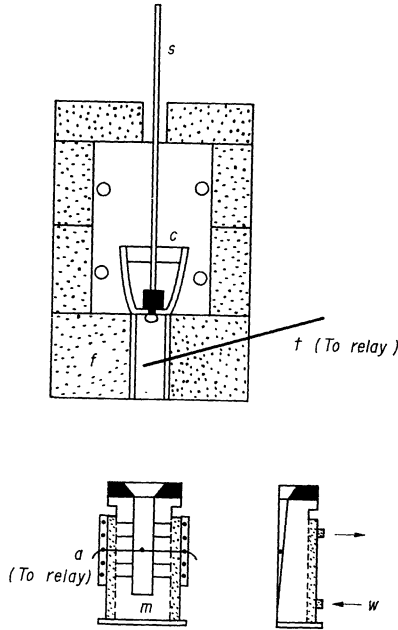


Fig. 1 Schematic representation of the apparatus.  
 s : Stopper c : Crucible f : Furnace  
 t : Trigger m : Copper mould  
 a : AC thermocouple w : Cooling water

### III. Results and Discussion

#### 1. Calculation of cooling rate

The heat issue from a molten metal cast into a mould to cooling water depended on the over-all heat transfer coefficient; it was influenced by the heat conduction in the molten metal and in the mould and by the heat transfers from the molten metal to the mould and from the mould to cooling water. In this experiment, therefore, heterogeneous nucleation in the supercooled molten alloy occurred not in the inner elements as impurities in the molten metal, but at the surface of the mould wall, because the cooling effect at the mould wall was greater than that in the impurities in the molten metal. Then the cooling process was examined under the following conditions; (a) the temperature gradient and the direction of heat flow were perpendicular to the mould wall, (b) the over-all heat transfer coefficient was not changed in the testing temperature range of all castings, (c) the temperature of cooling water in the mould was kept constant.

Under the above conditions, a small cylindrical element to be perpendicular to the mould wall was assumed, then the rate of heat issue was given as

$$Q = -V \times \rho \times C_p \times \frac{dT}{dt} = h \times A \times (T_1 - T_2). \quad (1)$$

From (1), the solution was obtained,

$$h = -2.303 \times \rho \times C_p \times \frac{V}{A} \times \frac{d \log E}{dt}. \quad (2)$$

The following equation was derived from (2) and (1)

$$v = 2.303 \times (T_1 - T_2) \times \frac{d \log E}{dt}. \quad (3)$$

$Q$  = rate of heat issue (cal/sec),  $V$  = volume of element

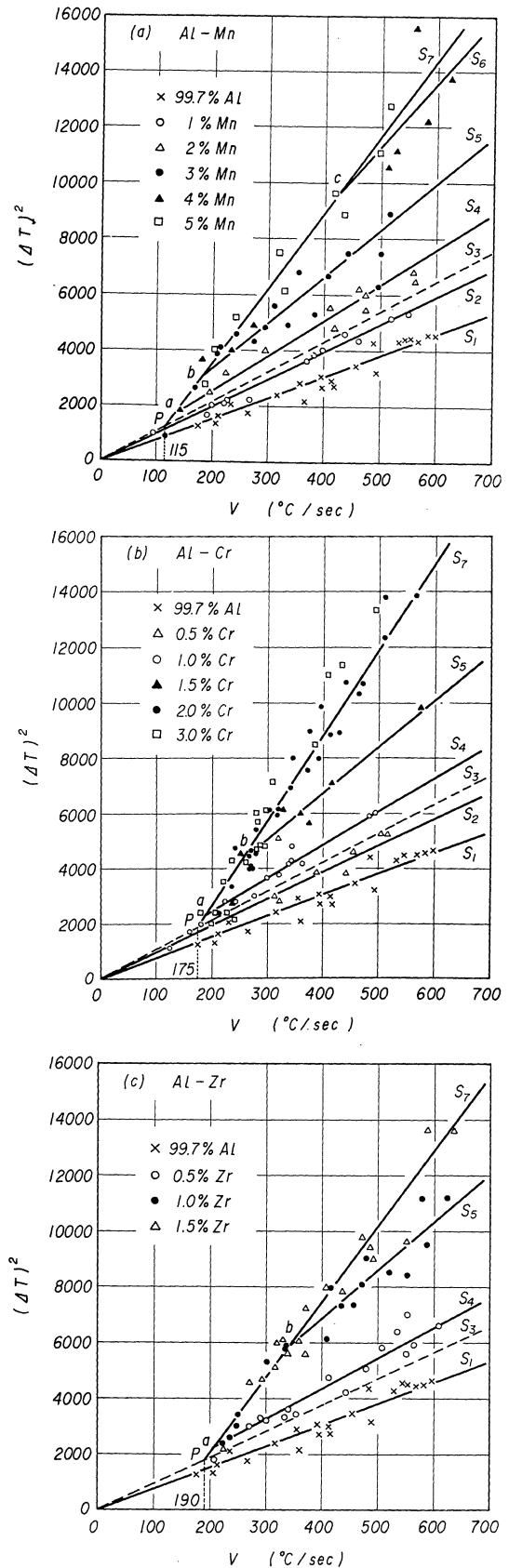


Fig. 2 Square of supercooling vs cooling rate for Al-Mn, Al-Cr and Al-Zr alloys.

( $\text{cm}^3$ ),  $\rho$  = density of molten metal ( $\text{g}/\text{cm}^3$ ),  $h$  = over-all heat transfer coefficient ( $\text{cal}/\text{cm}^2 \text{ } ^\circ\text{C sec}$ ),  $v$  = cooling velocity ( $^\circ\text{C}/\text{sec}$ ),  $E$  = relative thermo-electromotive force,  $C_p$  = specific heat of molten metals ( $\text{cal}/\text{g}^\circ\text{C}$ ),  $A$  = area of element being in contact with the mould wall ( $\text{cm}^2$ ),

$t$  = time (sec),  $T$  = temperature of molten metal ( $^{\circ}\text{C}$ ),  $T_1$  = temperature when molten metal contacted to the mould wall ( $800^{\circ}\text{C}$ ),  $T_2$  = temperature of cooling water ( $^{\circ}\text{C}$ ).

## 2. Relation between supercooling and cooling rate

The supercooling degree was obtained from the cooling curves by establishing the solidus temperature of the alloys as a standard and the cooling rate was then calculated from the above equation. The relations between cooling rate and supercooling degree in Al-Mn, Al-Cr and Al-Zr binary alloys of various alloying concentration are shown in Fig. 2. As shown in Fig. 2, two groups of straight lines were found; one was  $OS_1$ ,  $OS_2$ ,  $OPS_3$ ,  $aS_4$ ,  $bS_5$  and  $cS_6$  and the other was  $PabcS_7$ . In the former group, a square of the supercooling degree was proportional to the cooling rate at a certain alloy composition and the supercooling degree increased with increasing alloying element at a certain cooling rate. On the contrary, it was not so in the latter. Such a relation between the supercooling degree and the cooling rate was found in aluminium and its alloys having elements up to the maximum solid solubility in an equilibrium state as shown by straight lines  $OS_1$ ,  $OS_2$  and  $OS_3$ . The same relation was shown in the alloys solidified as a super-saturated solid solution when they contained more elements than the equilibrium solubility limit, as shown by  $aS_4$ ,  $bS_5$  and  $cS_6$ . The line  $PS_7$  was shown to be the lowest limit of the above relation.

The above results in Fig. 2 are schematically represented in Fig. 3. The solidification structures were shown as follows: The line (1) was structure of pure aluminium, the line (2) was that of the solid solution having a composition of the maximum solid solubility in an equilibrium state, the region (3) was that of the completely super-saturated solid solution primarily solidified in alloys having more element than the

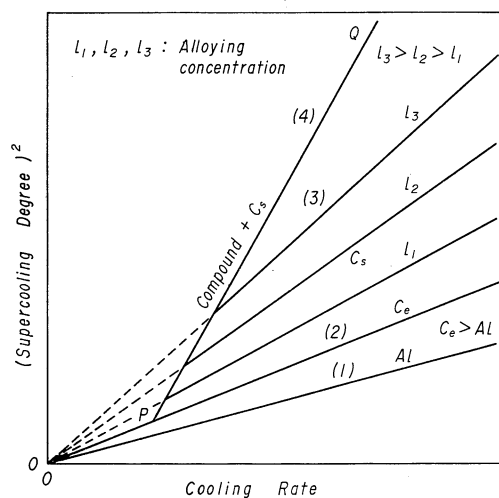


Fig. 3 Schematic illustration of relation between supercooling degree and cooling rate with increasing alloying element in aluminium alloys solidified easily to the structure of supersaturated solid solution.  
 $C_e$ : solid solution with the maximum equilibrium solid solubility  
 $C_s$ : super-saturated solid solution over the maximum equilibrium solid solubility

equilibrium solid solubility limit, and the line (4) was a mixed structure of the primarily crystallized intermetallic compound and the super-saturated solid solution. The primary compounds became finer and less with increasing cooling rate and super cooling degree (Photo. 1). The minimum cooling rate for obtaining the super-saturated solid solution beyond the maximum value of the equilibrium solid solubility limit was at the point P, i.e.  $115^{\circ}$ ,  $175^{\circ}$  and  $190^{\circ}\text{C}/\text{sec}$  in Al-Mn, Al-Cr and Al-Zr respectively.

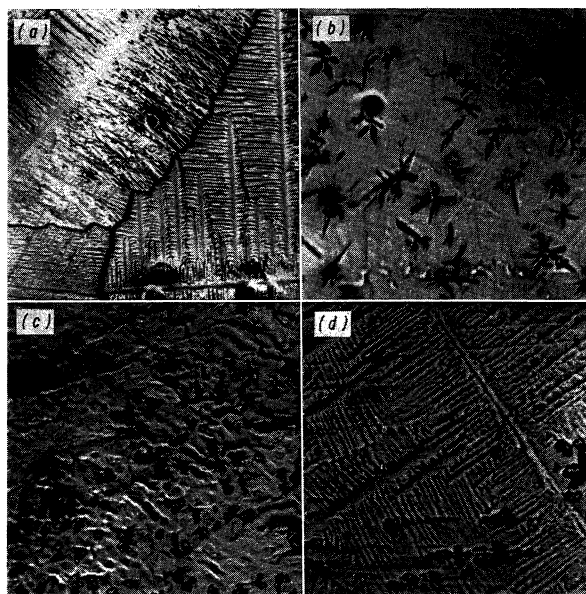


Photo. 1 Photomicrographs of the surface structures of specimens of Al-Cr alloy by rapid solidification  
 (a) completely super-saturated solid solution (in the range  $C_s$  in Fig. 3)  
 $\Delta T$ :  $78^{\circ}\text{C}$ ,  $v$ :  $495^{\circ}\text{C}/\text{sec}$  for Al-1%Cr ( $\times 175 \times 4/5$ )  
 (b)(c)(d) super-saturated solid solution and compounds (on the line PQ in Fig. 3) ( $\times 175 \times 4/5$ )  
 (b)  $\Delta T$ :  $64^{\circ}\text{C}$ ,  $v$ :  $270^{\circ}\text{C}/\text{sec}$  for Al-2% Cr  
 (c)  $\Delta T$ :  $89^{\circ}\text{C}$ ,  $v$ :  $393^{\circ}\text{C}/\text{sec}$  for Al-2% Cr  
 (d)  $\Delta T$ :  $111^{\circ}\text{C}$ ,  $v$ :  $509^{\circ}\text{C}/\text{sec}$  for Al-2% Cr

As mentioned above, the relation between supercooling degree and cooling rate was shown by the following equation on alloys solidified as a solid solution only [straight lines (1), (2) and region (3) in Fig. 3]:

$$\Delta T^2 = K_1 \times v \quad (4)$$

Such a relation was similar to that<sup>(7)</sup> between the degree of supercooling and solidification time.

And the cooling range for the solidification of compounds as primary crystallization was indicated by the following equation [(4) in Fig. 3]:

$$\Delta T^2 = K_2 \times v + K_3 \quad (K_2, K_3: \text{constant}). \quad (5)$$

As shown in Fig. 3, there was the limit in the cooling condition for super-saturation with increasing alloying content. From eqs. (4) and (5), the value of  $K_1$  was obtained under a definite value of cooling rate and the super-saturation degree at a certain cooling rate was derived from the relation<sup>(8)</sup> between the amount of solid

(7) K. A. Jackson: *Liquid Metals and Solidification*, ASM, (1958), p. 174.

(8) R. Ichikawa, T. Ohashi and T. Ikeda: *Summary of Lectures of 37th Lecture Meeting of Japan Institute of Light Metals* (1969), p. 41.

solubility and  $K_1$ . Then the relation between the super-saturation degree ( $C/C_e$ ) and the cooling rate ( $^{\circ}\text{C}/\text{sec}$ ) was given as shown in Fig. 4.

$C$  = component of super-saturated solid solution under various cooling conditions.

$C_e$  = maximum equilibrium solid solubility.

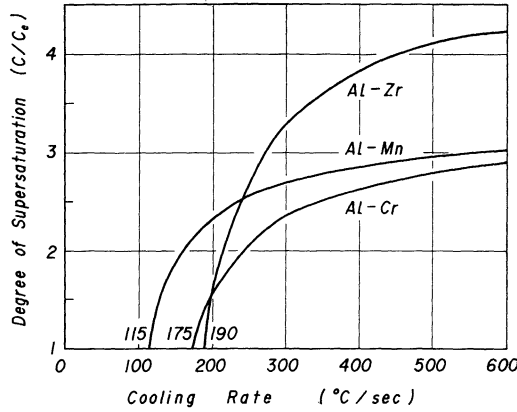


Fig. 4 Variation in the degree of supersaturation with cooling rate.

As shown in Fig. 4, the super-saturation began over a definite value of cooling rate and increased markedly with the cooling rate up to about  $400^{\circ}\text{C}/\text{sec}$ , beyond which it gradually increased. The order of the initiation of super-saturation on the cooling rate was Al-Mn, Al-Cr and Al-Zr.

These changes were supposed to be due to the diffusion of solute atoms in molten aluminium and to the chemical interaction between solute and aluminium atoms. The cooling rate for the initiation of super-saturation was regarded as being dependent on the diffusion rate of solute atoms. In other words, when the growth rate of the embryo in which solute atoms were above the maximum equilibrium solubility limit became higher than the diffusion rate of solute atoms, the initiation of the super-saturation became much easier. And with more solute atoms in the embryo, the chemical affinity between solute and aluminium atoms was more effective than the diffusion of solute atom, thereby the marked increase of the supersaturation degree changed to a gradual increase at a higher cooling rate in the order<sup>(9)~(12)</sup> of the chemical interaction of aluminium with Mn, Cr and Zr (Fig. 4).

From the above results, metastable phase diagrams of Al-Mn, Al-Cr and Al-Zr alloys under different cooling conditions are shown in Fig. 5. As shown in the figure, the melting point of aluminium and the solidus temperature of the  $\alpha$ -phase which was coincident to the liquidus and temperatures of eutectic and peritectic went down by following the relation of  $\Delta T^2-v$  (in Fig. 2) and the super-saturated solid solution was obtained. The final

cooling rate for obtaining the super-saturated solid solution with increasing alloying element was regarded as

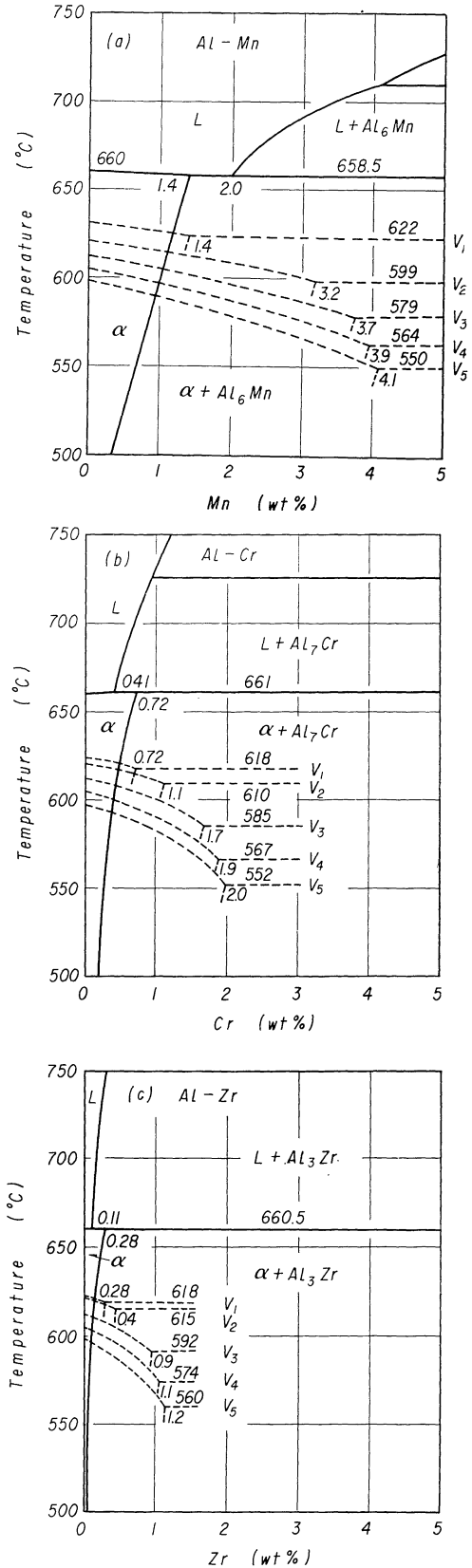


Fig. 5 Metastable phase diagrams of Al-Mn, Al-Cr and Al-Zr systems.  
 $V_1$ : minimum cooling rate formed super-saturated solid solution  
 $V_2, V_3, V_4, V_5$ : 200°, 300°, 400° and 500°C/sec, respectively

(9) L. Darken and R. Gurry : *Physical Chemistry of Metals*, McGraw-Hill, (1953), p. 79.  
 (10) R. P. Agarwala, S. P. Muraka and M. S. Anand : *Acta Met.*, 12 (1964), 871.  
 (11) T. S. Lundy and J. F. Murdock : *J. Appl. Phys.*, 13 (1962), 1671.  
 (12) G. Falkenhagen und W. Hofmann : *Z. Metallk.*, 43 (1952), 69.

the one where  $K_1$  was coincident with  $K_2$  [eqs. (4) and (5)].

#### IV. Conclusion

The solidification processes at various cooling rates were investigated with Al-Mn, Al-Cr and Al-Zr alloys which were easily solidified to super-saturated solid solution structures by rapid cooling.

(1) The square of supercooling degree was proportional to the cooling rate in aluminium and aluminium alloys which were solidified to the structures of completely

super-saturated solid solutions by rapid cooling over a definite rate and the supercooling degree increased with increasing alloying element.

(2) The minimum cooling rate for obtaining the solidified structure of a super-saturated solid solution at a composition over the maximum solid solubility limit in an equilibrium state was  $115^\circ$ ,  $175^\circ$  and  $190^\circ\text{C}/\text{sec}$  on Al-Mn, Al-Cr and Al-Zr respectively.

(3) Metastable phase diagrams were proposed on Al-Mn, Al-Cr and Al-Zr alloys under several cooling conditions.

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