Significance of the Solidifying Zone on the Ingot Solidification*

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Synopsis

The solidifying zone, which is composed of solid and liquid phases at the solidification front, is very important to understand the solidification mechanism of the ingot. This zone has therefore been examined on the basis of the behaviour of the solute-rich liquid between dendrites. The fundamental analysis made for the solidifying zone has been applied to explain the solidification phenomena of steel ingots. The results obtained are summarized as follows:

The effective distribution coefficient, k^* , is represented by

$$k^* = 1 - EU$$

where E is an experimental constant and U is the flow velocity of bulk liquid. Thus k^* depends only on U . However, there is a minimum in the value of k^* . The minimum effective distribution coefficient, k_m^* , is expressed by

$$k_m^* = 1 - Sp(1 - k_0)$$

where Sp is the critical fraction of solid above which the liquid is completely entrapped by the solid and k_0 is the equilibrium distribution coefficient. Since the value of k_m^* is 0.45 for Al-4wt%Cu alloy, the value of Sp is calculated to be 67%. This agrees well with the value of Sp actually observed for carbon steel, 65 to 69%. Assuming that the value of Sp is equal to 0.67, the minimum effective distribution coefficients calculated for the alloying elements in steel are 0.42 for carbon, 0.81 for manganese, 0.37 for phosphorus, and 0.34 for sulphur respectively. These values agree well with the minimum effective distribution coefficients observed for the rim-zone of rimming ingots. From these, it is evident that the macrosegregation in the rim-zone of rimmed steel ingots is determined only by the degree of washing against the solidifying zone with the turbulent flow of bulk liquid.

I. Introduction

The dendritic crystals are generally formed during solidification, where the morphology of growing crystals is determined by heat transfer and by crystallographic and physical properties of the alloy. The solidification proceeds with the development of the dendritic aggregates. On the other hand the fluid motion of bulk liquid is caused by the phenomena taken place during the solidification of steel ingot such as free convection, rimming action with the evolution of CO gas, and so on. Thus the relation between the dendrite morphology and the fluid motion should not be neglected in the discussion of the segregation in steel ingots.

The theoretical equation introduced to the assumption that the solidification interface is planar, can be adopted for the controlled solidification under the conditions of a steep temperature gradient and a constant rate of solidification,¹⁻⁴⁾ e.g. in the case of zone melting. However, it can not be applied to the solidification of commercial steel ingot, which is naturally solidified in a mold.⁵⁻⁷⁾

A region, in which the dendritic aggregates are in equilibrium with the neighbouring liquid, is formed during the solidification of alloy according to the mutual relation between the temperature profile of the region and the difference in the liquidus and the solidus temperatures. The region is called as "the solidifying zone" in the present paper. In the current investigation the fundamental analysis made for the solidifying zone is also applied to the solidification of steel ingots. A model experiment is firstly performed on the effect of washing against the solidifying zone with the fluid flow of bulk liquid. The segregation behaviour and the solidification mechanism of steel ingots are then discussed on the basis of the results obtained.

II. Fundamental Concept of the Solidifying Zone

A region which is composed of the dendrites and the interdendritic liquid is generally formed during the solidification of alloy. This region of partial solidification is called as "the solidifying zone" in this paper. In this chapter the difference between the solidification with the planar interface and that with the solidifying zone is discussed on the basis of the experimental results obtained.

It has been accepted that the transition from the columnar to the equiaxed zone in an ingot can be explained by considering the region of constitutional supercooling, which is determined from the mutual relation between the gradients of temperature and concentration at the solidification front based on the assumption that the solid/liquid interface is planar. In the solidification with a planar interface, the solute concentration of the liquid at the solidification front increases with increasing rate of solidification, and the solute concentration of the solid at the interface is determined from that of the neighbouring solute-rich liquid according to the phase diagram. Thus the distribution of the solute concentration of the solid is smooth so long as the rate of solidification does not change rapidly. Therefore the microsegregation does not occur. It seems that there is no freezing range in the solidification with a planar interface, since the planar interface advances continuously at the liquidus temperature which corresponds with the solute concentration of the liquid.

However, the following four characteristics are seen in the solidification of commercial steel ingots.

- (1) There are such freezing ranges as F_1 and F_2

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Fig. 1. A schematic illustration of the changes of the temperature profile and the solidifying zone with the progress of solidification. The subscripts "1" and "2" show the temperature profile, G , and the solidifying zone, F , in the initial and later stages of solidification respectively.

shown in Fig. 1 so long as the temperature gradient does not become extremely steep at the solidification interface.

(2) Some difference between the liquidus and the solidus temperatures is observed in the cooling curve for each part of the ingot.

(3) The crystal grows with the formation of dendritic aggregates not only in the chill and the columnar zones but also in the branched columnar and the equiaxed zones. Schürmann and Grotschel⁸⁾ showed that there is a dendrite structure even in the rimmed steel ingots containing 0.049–0.083% C, using a special etching method developed by Hultgren and Phragmén.⁹⁾

(4) Results of the concentration analyses with an electron probe microanalyzer show that the solute concentration changes rapidly in the dendrite arm spacings.

As described above, many contradictions are disclosed between the solidification which proceeds with a planar interface and the solidification of commercial steel ingots. Therefore, the existence of the solidifying zone which is the most important for the solidification of steel ingots may be neglected if the theory for the solidification with a planar interface is applied to the solidification of steel ingots.

The difference in the temperatures between the solid and the liquid phases in the solidifying zone is considered to be very small because of their high heat conductivities. Since the solute concentration of the liquid in the solidifying zone is supposed to be almost in equilibrium with that of the neighbouring solid, the concentration gradient can be estimated from the temperature gradient. The thin solute-rich liquid zone of 10^{-1} to 10^{-3} cm in thickness is formed in the solidification with a planar interface due to

a steep temperature gradient at the solid/liquid interface, while the temperature gradient in the solidifying zone is very small because the thickness of the zone is more than 1 cm at the initial stage of solidification¹⁰⁾ and increases as the solidification proceeds. Therefore such constitutional supercooling as in the solidification with a planar interface may be difficult to occur in the solidification with a solidifying zone. This must be taken into account for the discussion on the change in the morphology from the columnar to the free crystals. The concentration distribution and the thickness of the solute-rich liquid zone in the solidification with a planar interface are determined by the degree of fluid motion of the bulk liquid passing through the vicinity of the interface. However, the liquid at the inside of the solidifying zone becomes to show a different solute concentration with the increase of the fraction of solid, since the fluid motion can not be taken place at the position over a limited distance from the tip of the zone. Thus free convection is caused in the solidifying zone owing to the difference in the concentrations between the solute-rich liquid and the neighbouring one.¹¹⁾ This behaviour of the solute-rich liquid in the solidifying zone becomes important for the discussion of the inverse V segregation of killed steel ingots.¹²⁾

III. Effect of Washing against the Solidifying Zone with the Fluid Motion of Bulk Liquid

Effect of washing against the solidifying zone by the fluid flow of bulk liquid is important to understand the segregation behaviours during the solidification of steel ingots. Thus the degree of stirring of the remaining liquid during solidification is supposed to characterize whether the steel ingot will be rimmed or killed. Theoretical analysis on the basis of the experimental results obtained by using a special method of solidification has been made in order to clarify the effect of the fluid flow of bulk liquid on the solidifying zone.^{13,14)}

1. Experimental Consideration on the Effective Distribution Coefficient

1. Experimental Procedure

There are some different ways in stirring, for example, the electromagnetic stirring, the stirring by high frequency induction, and so on. But the degree of stirring can not be quantitatively shown by these methods. Therefore, the well-known Taylor's vortex method with two concentric cylinders was used to change the flow velocity of bulk liquid. As the outer cylinder was at rest and the water-cooled inner cylinder was rotating, the solidification proceeded from the inner to the outer side. It was shown that this cooling method is very effective for the study of the segregation behaviour of the ingot, since the solute concentration of the remaining liquid does not increase so much in the later stage of solidification and the gravity segregation does not occur owing to the turbulence and the centrifugal force.

As the sample, Al-4wt%Cu alloy was used. A schematic view of the experimental apparatus is shown

in Fig. 2. The outer cylinder used for melting was a graphite crucible of 12 cm in I.D., 14 cm in height, and 1 cm in thickness. A pipe of 2 cm in diameter made of copper or steel was used as the inner cylinder. The inner cylinder was cooled by flowing water at the rates of 1/6 and 1/18 l/sec during solidification. The inner cylinder was rotated at the rates of 90, 420, 650, and 750 rpm respectively. The rate of solidification was measured from the direct observation of the thickness of solidified layer on the upper surface of the ingot.

When Al-4wt%Cu alloy of about 3 kg was melted in the crucible the height of the melt became 10 cm. After the molten alloy was sufficiently agitated at 700°C, the heat supply for the melt was stopped. Then the water-cooled inner cylinder was immersed to 4 cm below the upper surface of the melt and rotated at each cycle of rotation as soon as possible so that the solidification proceeded from the inner to the outer side.

2. Experimental Results and Analysis

In this section it will be discussed what determines the effective distribution coefficient, k^* , in the solidification which proceeds with the solidifying zone. Burton *et al.* presented the effective distribution coefficient theoretically as follows:¹⁾

$$k^* = \frac{k_0}{k_0 + (1 - k_0) \exp(-V\delta/D)} \quad (1)$$

where k_0 is the equilibrium distribution coefficient, D the diffusion coefficient of solute, δ the thickness of the

diffusion layer at the planar interface, and V the rate of solidification. In Eq. (1), the factors controlling k^* are δ and V when k_0 is constant.

The thickness of the laminar sub-layer defined on the basis of hydrodynamics is described as δ_l , in order to distinguish δ from δ_l . Now let us examine the mutual relation between δ and δ_l . Substituting $k_0 = 0.16$,¹⁵⁾ $D = 7 \times 10^{-5} \text{ cm}^2/\text{sec}$ ¹⁶⁾ and the observed values of k^* and V into Eq. (1), the value of δ at each part of the ingot can be calculated. As the result, the value of δ remained approximately constant in all the parts of the ingot and the mean value of δ is $6.0 \times 10^{-3} \text{ cm}$.

According to Nikuradse,¹⁷⁾ δ_l is expressed as follows:

$$\delta_l = 5\nu \sqrt{\rho'/\tau} \quad (2)$$

where ν is the kinematic viscosity, ρ' the density, and τ the shearing stress. Taylor made the experiment on the velocity of the fluid flow between two concentric cylinders and found that the value of $U \times r$ was half the value of $U_s \times r_o$, where U was the flow velocity, r the distance from the center of the inner cylinder to the fluid, U_s the peripheral velocity of the inner cylinder, and r_o the radius of the inner cylinder.¹⁸⁾ Therefore, the shearing stress is given by

$$\tau = \frac{\mu U_s}{2\delta_l} \quad (3)$$

where μ is the viscosity. Using Eqs. (2) and (3), δ_l is rewritten as follows:

$$\delta_l = 50\nu/U_s \quad (4)$$

The value of ν is $2.3 \times 10^{-3} \text{ cm}^2/\text{sec}$,¹⁹⁾ and the value of U_s is estimated from both the thickness of the solidified ingot and the cycle of rotation per minute of the inner cylinder during solidification. Substituting these values into Eq. (4), the thickness of the laminar sub-layer is obtained.

The statistical examination¹³⁾ shows no correlation between the thickness of the diffusion layer, δ , and the thickness of the laminar sub-layer, δ_l . The value of δ is much greater than δ_l , e.g. the mean value of δ is five times larger than that of δ_l at $U_s = 100 \text{ cm/sec}$.

If δ is independent of the degree of stirring, U_s , the effective distribution coefficient of Eq. (1) should be expressed as a function of the rate of solidification. Figure 3 shows the relation between the effective distribution coefficient, k^* , the rate of solidification, V , and the peripheral velocity of the rotating solid surface, U_s , for Al-4wt%Cu alloy. It might be considered as if k^* were related to V . However, the detailed examination clearly shows that k^* depends only on U_s as shown in Fig. 4. The value of k^* decreases linearly with increasing U_s when U_s is decreased below 160 cm/sec, but remains constant at 0.45 when U_s is increased over 160 cm/sec.

As described above in the solidification with the fluid motion of bulk liquid k^* is independent of V but is a function of U_s or U only. The empirical equation is expressed as follows:

- 1 Molten alloy
- 2 Graphite crucible
- 3 Furnace
- 4 Copper or steel pipe for water-cooling
- 5 Scale for measurement of solidified shell
- 6 Motor
- 7 Belt
- 8 Flow meter
- 9 Gear pump
- 10 Ball bearing
- 11 Union

Fig. 2. Experimental apparatus used for the solidification with rotation of the liquid

Fig. 3. Relation between effective distribution coefficient, k^* , and rate of solidification, V , for 5 levels of U_s in Al-4wt%Cu alloy (U_s is peripheral velocity of the rotating solid surface.)

Fig. 4. Relation between the effective distribution coefficient, k^* , and the peripheral velocity of the rotating solid surface, U_s , for Al-4wt%Cu alloy

$$\begin{aligned} \text{For } U < 80 \text{ cm/sec} \quad k^* &= 1 - 6.86 \times 10^{-3} U \quad \dots\dots(5-a) \\ \text{For } U \geq 80 \text{ cm/sec} \quad k^* &= 0.45 \quad \dots\dots(5-b) \end{aligned}$$

Thus it is found that Eq. (1), obtained by Burton *et al.* on the solidification with a planar solid/liquid interface, no longer holds true in the ingot solidification which proceeds with the solidifying zone. The effective distribution coefficient in the solidifying zone will be discussed theoretically in the following section.

2. Theoretical Consideration on the Solidifying Zone and the Effective Distribution Coefficient

1. Classification of the Solidifying Zone

The solidifying zone can be divided into two zones, p and q according to the previous observation.¹¹⁾ Both the p and q zones are composed of solid and liquid phases. In the p zone the liquid is entrapped by the solid. Thus the concentration of solute in the p zone remains unchanged after solidification. On the other hand, the solid phase exists within the liquid in the q zone. Furthermore, the q zone is subdivided into q_1 and q_2 zones. In the q_1 zone the solid phase forms dendrite skeleton and the liquid can flow through the dendrite arm spacings. The q_2 zone is the so-called pasty zone containing free dendrites.

The remaining liquid in the p zone becomes the origin of dendrite segregation and nonmetallic inclusions, since the solute concentration of the remaining liquid is sufficiently increased to form nonmetallic inclusions during solidification. Thus the behaviour of remaining liquid becomes as the most important factor for the discussion concerning the formation mechanism of nonmetallic inclusions. The average solute concentration of the p zone, $\bar{C}_p$, must be equal to that of the solid zone, $\bar{C}_s$, since it remains constant after solidi-

Fig. 5. A schematic illustration of the temperature and the concentration distributions near the solid/liquid interface in binary alloys

fication. Therefore, the p zone can be considered as a virtual solid zone on the discussion of the effective distribution coefficient, k^* . Only the q zone will be examined in detail later.

2. Boundary between the p and q Zones

In order to obtain the boundary condition between the p and q zones let us examine the solidification during which the solidifying zone is completely washed out by the fluid motion of bulk liquid. As the dashed line, T_o-d , is a virtual solidus line in Fig. 5, it shows the critical fraction of the solid, Sp , above which the q zone changes to the p zone. The average solute concentration of the p zone, $\bar{C}_p$, is expressed as follows:

$$\bar{C}_p = \delta S k'_o C_{L,o} + (Sp - \delta S) k_o C_{L,o} + (1 - Sp) C_{L,o} \quad \dots\dots(6)$$

where δS is the fraction of the solid initially formed when the melt is undercooled by δT_c , k'_o the non-equilibrium distribution coefficient, $C_{L,o}$ the initial solute concentration of the liquid, and k_o the equilibrium distribution coefficient. Since the concentration $\bar{C}_p$ is equal to the concentration $\bar{C}_s$, the minimum effective distribution coefficient, k_m^* , is expressed by

$$k_m^* = \bar{C}_p / C_{L,o} = 1 - Sp(1 - k_o) + \delta S(k'_o - k_o) \quad \dots\dots(7)$$

The critical fraction of solid, Sp , above which the q zone changes to the p zone, is also represented by,

$$Sp = \frac{(1 - k_m^*) + \delta S(k'_o - k_o)}{1 - k_o} \quad \dots\dots(8)$$

The term of $\delta S(k'_o - k_o)$ is supposed to be very small as compared with that of $(1 - k_m^*)$ in Eq. (8) except in the case of a comparatively large degree of undercooling at the initial stage of solidification. Thus the minimum effective distribution coefficient is approximately given by

$$k_m^* = 1 - Sp(1 - k_o) \quad \dots\dots(9)$$

The value of Sp is estimated to be over 50% because it is evident that the solute-rich liquid can flow and

diffuse at $Sp=0.5$ in the previous study for Al-Cu alloy¹¹⁾ made by the authors.

3. Temperature Profile in the q Zone

In this section, the following five assumptions are made:

(1) The heat conductivity and the specific gravity of the q zone are the mean values between those of the solid and the liquid.

(2) The temperature difference between the solid and the liquid is negligible in the solidifying zone because of their high heat conductivities.

(3) The latent heat of fusion is considered to be the change in the specific heat.

(4) The solidification begins slightly below the equilibrium liquidus temperature.

(5) The fluid flow of molten metal is the so-called "slug flow" since the heat transfer due to the turbulent mixing is negligible on account of the high heat conductivity even when turbulence is caused in the q_1 zone by the application of stirring.²⁰⁾

Now, the following calculation is made in order to obtain the temperature profile of the zone. If x is the distance along the direction of solidification and the origin is always taken at the point of the virtual solidus line, that is $x=0$ at $T'=T'_s$ in Fig. 5, the equation for steady-state heat flow in the q zone is expressed as follows:

$$\frac{d^2 T'}{dx^2} + \frac{V}{\alpha'} \frac{dT'}{dx} = 0 \quad \dots\dots\dots(10)$$

where V is the rate of solidification, α' the thermal diffusivity of the q zone. The boundary conditions are

$$\left. \begin{array}{l} x=0: \quad T' = T'_s \\ x=h: \quad T' = T_E - \delta T_c \end{array} \right\} \quad \dots\dots\dots(11)$$

Assuming that T' is finite even at $h=\infty$, the solution of Eq. (10) is given by

$$T'(x) = T'_s + \frac{\Delta T_2}{1 - \exp(-Vh/\alpha')} \{1 - \exp(-Vx/\alpha')\} \quad \dots\dots\dots(12)$$

where

$$\Delta T_2 = T_E - \delta T_c - T'_s \quad \dots\dots\dots(13)$$

and

$$\begin{aligned} \alpha' &= \lambda / \{ \rho \bar{C}_p + \rho(Sp - \delta S)L / \Delta T_2 \} \\ &\approx \lambda \Delta T_2 / \rho(Sp - \delta S)L \quad \dots\dots\dots(14) \end{aligned}$$

Inserting $T_L = T_a$ at $x=\infty$ and $T_L = T_E - \delta T_c$ at $x=h$ into the equation similar to Eq. (10), the temperature profile of the bulk liquid, $T_L(x)$, is expressed as follows:

$$T_L(x) = T_a - \Delta T_1 \exp V(h-x)/\alpha \quad \dots\dots\dots(15)$$

$$\Delta T_1 = T_a - T_E + \delta T_c \quad \dots\dots\dots(16)$$

4. Thickness of the q_1 Zone

The starting point of solidification, $x=h$, in Fig. 5 is determined from the boundary condition which can be obtained from Assumption 3 in the previous section

$$\left(\frac{dT'}{dx} \right)_{x=h} - \left(\frac{dT_L}{dx} \right)_{x=h} = V \rho L \delta S / \lambda \quad \dots\dots\dots(17)$$

where δS is the fraction of the solid initially formed at $x=h$ when the molten alloy is undercooled by δT_c , as described above. On the basis of the equilibrium phase diagram the relation between δS and δT_c is represented by

$$\delta S = \delta T_c / (a C_{L0} + \delta T_c)(1 - k_0) \quad \dots\dots\dots(18)$$

where C_{L0} is the initial solute concentration of the liquid.

From the relation between the degree of undercooling and the solute concentration of the primary crystal in Al-4wt%Cu alloy it is obvious that the solute concentration of the primary crystal is nearly consistent with that of the solidus line in the equilibrium phase diagram when the melt is undercooled by less than 15°C.²¹⁾ Thus the fraction of solid of δS is calculated from Eq. (18) if the molten alloy is undercooled by less than 15°C.

Using Eqs. (12), (15), and (17), the thickness of the q_1 zone is expressed as follows:

$$h = \frac{\alpha'}{V} \ln \left(1 + \frac{\Delta T_2 / \alpha'}{\rho L \delta S / \lambda + \Delta T_1 / \alpha} \right) \quad \dots\dots\dots(19)$$

5. Fluid Flow in the q_1 Zone with Stirring

The fluid flow in the q_1 zone will only be discussed in this section. It is easy to examine the q_2 zone on the basis of hydrodynamics, since the q_2 zone can be treated as a kind of liquid. No experiment on the fluid flow in the q_1 zone having a complicated structure of dendrites has been made up to present. However, this can be understood to some extent from the experimental results obtained by Nikuradse with coarse sand grains glued on the surface²²⁾ as described below.

When all protrusions on the surface of solid are contained within the laminar sub-layer, the rough surface is hydraulically smooth. When protrusions extend partly outside the laminar sub-layer, the transitional turbulence is caused by them. When all protrusions reach outside of the laminar sub-layer, the protrusions experience the friction fully. The height of protrusion, h , is only a roughness factor in the above case. However, the distance between protrusions, b , must also be taken into consideration as one of the roughness factors. For example, from the experiment on the sphere glued to the surface it was found that the rough surface became hydraulically smooth with the decrease of the distance between protrusions when the distance was very small.²³⁾

Accordingly, in the Nikuradse's experiment it is only shown that turbulence can be caused in the q_1 zone by stirring. The following proposition may be given in the current work, that is, turbulence does not occur in the whole range of q_1 zone and can not penetrate over a limited distance from the tip of the protrusions, Δh , when b/h is less than unity. From the photographic observation of the macrostructure in the columnar zone of an Al-Cu alloy, it is estimated that

the value of b/h is considerably smaller than unity. Although Δh and the factors controlling it have never been observed or evaluated, it may be considered that Δh is proportional to b and is the order of the magnitude of b . The value of Δh is treated as an experimental constant here and will be examined from the comparison with their experimental results later.

6. Transport of Solute by Stirring

The mass (or momentum), which is transported per unit time by turbulent mixing, is expressed as follows:

$$Q = -A \left(\frac{dW}{dx} \right) \dots\dots\dots(20)$$

where W is the mass (or momentum) which is transported by turbulent mixing, and A the turbulent diffusivity. The term of A is called as the *turbulent diffusivity of mass* (A_D) for the transport of mass, and as the *turbulent diffusivity of momentum* (A_τ) for the transport of momentum.

The transports of mass and momentum due to diffusion and viscous flow are generally negligible small in the case of turbulent flow. Since A_D is approximately equal to A_τ in the turbulent flow,²⁴⁾ the solute concentration of the liquid, C_L , is proportional to the flow velocity, U . The above condition is supposed to hold true in the bulk liquid outside of the q_1 zone, i.e. $x > h$ in Fig. 5.

The distribution of the solute concentration of the liquid within the q_1 zone is determined by the temperature profile of the zone. Since the diffusion distance is decreased in the vicinity of $x=0$ and the diffusion by turbulent mixing is violent in the vicinity of $x=h$ in Fig. 5, the solute concentration of the liquid along the direction perpendicular to the x axis is supposed to be almost uniform. So the concentration gradient of solute in the liquid of q_1 zone will be produced along the x direction. Thus it is approximately expressed as follows:

$$\frac{dC'_L}{dx} = - \frac{dT}{dx} / a \dots\dots\dots(21)$$

The liquid of initial concentration C_{L0} is changed into the solid of C'_s and the liquid of C'_{L0} when the molten alloy is undercooled by δT_c . The ratio of the solid area to the liquid area at the hypothetical interface of $x=h$ in Fig. 5 is considered to be $\delta S/(1-\delta S)$. The solute concentration of the liquid is C'_{L0} in the area which is adjacent to the solid surface and C_{L0} in the area which is apart from the solid surface. Thus the average solute concentration of the liquid at $x=h$ is represented by

$$\left. \begin{aligned} \overline{C'_{L0}} &= C_{L0}(1-\delta S) + C'_{L0}\delta S \\ &= C_{L0} + \delta C \delta S \approx C_{L0} \end{aligned} \right\} \dots\dots\dots(22)$$

where

$$\delta C = C'_{L0} - C_{L0} \dots\dots\dots(23)$$

7. Effective Distribution Coefficient

Columnar crystals were observed in the macrostructure of Al-4wt%Cu alloy in this experiment. So, the effective distribution coefficient in the solidification which is accompanied by the q_1 zone with columnar protrusions, has been examined in order to

analyse the experimental results. When turbulence is caused in the q_1 zone by stirring, the quantity of solute, which is transported per unit time outside of the q_1 zone by the turbulent mixing at $x=h$, is expressed from Eqs. (20) and (21) as follows:

$$(\dot{m})_{x=h} = \frac{A_D}{a} \left(j \frac{dT}{dx} \right)_{x=h} \dots\dots\dots(24)$$

where j is the effective cross section for diffusion and so $(j)_{x=h} = 1 - \delta S$, as described above. With the advance of solidification, the quantity of solute, which is transported inside of the q_1 zone, is $V\overline{C'_{L0}} \approx VC_{L0}$ at $x=h$, while the quantity of solute, which is transported outside of the q_1 zone, is $V\overline{C_p} = V\overline{C_s}$ at $x=0$. Thus Eq. (24) is rewritten as follows:

$$V(C_{L0} - \overline{C_s}) = (1 - \delta S) \frac{A_D}{a} \left(\frac{dT}{dx} \right)_{x=h} \dots\dots\dots(25)$$

Inserting Eq. (12) into Eq. (25), the following equation is obtained.

$$1 - k^* = \frac{(1 - \delta S) A_D \Delta T_2 \exp(-Vh/\alpha')}{a C_{L0} \alpha' \{1 - \exp(-Vh/\alpha')\}} \dots\dots\dots(26)$$

It has been reported that A_τ is in proportion to the turbulent flow velocity, U ,²⁵⁾ and the width of mixing zone, Δh .²⁶⁾ Since $A_\tau = A_D$ under the condition of turbulence as described above, A_D is given by

$$A_D = B \Delta h U \dots\dots\dots(27)$$

where B is a constant determined on the basis of hydrodynamics.

Substituting α' of Eq. (14) into Eq. (19), the thickness of the q_1 zone is represented by

$$h = \frac{\lambda \Delta T_2}{\rho L (Sp - \delta S)} \ln(1 + Z) \dots\dots\dots(28)$$

where

$$Z = \frac{\rho L (Sp - \delta S) / \lambda}{\rho L \delta S / \lambda + \Delta T_1 / \alpha} \dots\dots\dots(29)$$

Using Eq. (28),

$$\exp(-Vh/\alpha') = \exp\{-\ln(1 + Z)\} = 1/(1 + Z) \dots\dots\dots(30)$$

Therefore, Eq. (26) is rewritten as follows:

$$1 - k^* = \frac{\rho B \Delta h L (1 - \delta S) (Sp - \delta S) U}{a C_{L0} \lambda Z} \dots\dots\dots(31)$$

It is confirmed that Δh and δS remain approximately constant in Eq. (31) except the cases of the initial and later stages of solidification and of the special conditions of slow cooling. Assuming that they are constant, all the factors but U in the right-hand side of Eq. (31) become constant. So, the effective distribution coefficient, k^* , is expressed as follows:

$$k^* = 1 - EU \dots\dots\dots(32)$$

where

$$E = \frac{\rho B \Delta h L (1 - \delta S) (Sp - \delta S)}{a C_{L0} \lambda Z} \dots\dots\dots(33)$$

Equation (32) shows that k^* decreases linearly with increasing U . It will be demonstrated later that there is a lower limit to the value of k^* in Eq. (32) because the solidifying zone can not be washed by the fluid motion of bulk liquid when the fraction of solid in the solidifying zone is increased to some extent. The above consideration agrees well with the experimental results of Eqs. (5-a) and (5-b).

8. Evaluation of the Factors Controlling k^*

Equation (32) is the solution for the infinite ingot under the steady state condition. Strictly speaking it is unreasonable to apply this equation for the case of a finite ingot, in which the solidification proceeds under the unsteady state condition. However, Eq. (32) may be adopted to obtain an approximate solution for the finite ingot except the vicinity of the inner and the outer cylinders.

The analytical calculation is compared with the experimental result. Reichardt reported $B=1.4 \times 10^{-2}$ for the free turbulence,²⁷⁾ and Karmán also presented $B=1.19 \times 10^{-2}$ for the flow along a smooth wall.²⁸⁾ Both values are approximately the same. The value of 1.2×10^{-2} is used here for B . The physical constants in Eq. (33) are quoted from the data of aluminum: $\lambda=0.334 \text{ cal/cm} \cdot \text{sec} \cdot ^\circ\text{C}$, where $\lambda=(\lambda_1+\lambda_2)/2$,²⁹⁾ $\lambda_1=0.247$ for the liquid at 700°C , and $\lambda_2=0.42$ for the solid at 600°C ,³⁰⁾ $c=0.259 \text{ cal/g} \cdot ^\circ\text{C}$ at 660° to 1000°C ,²⁹⁾ $\rho=2.38 \text{ g/cm}^3$,²⁹⁾ and $L=96 \text{ cal/g}$.²⁹⁾ From the equilibrium phase diagram of Al-Cu alloy the following values are obtained: $a=340/\rho \cdot ^\circ\text{C cm}^3/\text{g}$, $k_o=0.16$,¹⁵⁾ and $C_{Lo}=0.04 \text{ g/cm}^3$.

Then, the factors of ∂S , Sp , and Jh are determined on the basis of the experimental results and the analysis. The fraction of solid, ∂S , which is initially formed when it is undercooled by ∂T_c , is firstly examined. The degree of undercooling, ∂T_c , remained approximately constant at 4°C in a wide region of Al-4wt%-Cu alloy in this experiment. The value of ∂S is calculated to be 0.27 from Eq. (18).

In order to determine the value of the critical fraction of solid, Sp , above which the q zone changes to the p zone by Eq. (8), it is necessary to obtain the values of the minimum effective distribution coefficient, k_m^* , and the nonequilibrium distribution coefficient, k_o' . Equation (5-b) shows the value of k_m^* . It is reported that the value of k_o' for Al-4wt%-Cu alloy is 0.20.²¹⁾ Thus the value of Sp is calculated to be 0.67.

To determine the thickness of mixing zone, Jh , it is necessary to obtain the values of E and Z . Equation (5-a) shows the value of E . In this experiment it was also observed that the superheat, JT_1 , at the tapping time diminished when the solidification proceeded to the distance of 1 cm from the inner cylinder. When $JT_1=0$, the value of Z is calculated to be 1.44 from Eq. (29). Thus the value of Jh calculated becomes $5.9 \times 10^{-2} \text{ cm}$.

Since the mean interval between the columnar crystals, b , was measured to be $8.2 \times 10^{-2} \text{ cm}$ for the stirred ingot of this experiment, Jh is approximately equal to b as expected.

3. Application of Experimental Results to the Commercial Steel Ingots

1. Similarity of the Morphology and the Distribution of Dendrites between Steel and Al-Cu Alloy

For the discussion of the solidification mechanism and the segregation behaviour it is necessary to observe experimentally the morphology of solidification interface. The solidification interfaces have been observed for an Al-4wt%-Cu alloy and a carbon steel ingot, as shown in Photos. 1 and 2 respectively. The solidification interface shown in Photo. 1 (a) was formed as follows. A water-cooled pipe was immersed into the center of the melt. The solidification proceeded from the inner to the outer side. Then the water-cooled pipe with the solidifying zone was pulled up and rotated as soon as possible, to remove the re-

Photo. 1. The morphology of solidification interface for Al-4wt%-Cu alloy ingot
(a): $(\times 1) (\times 5/8)$, (b) and (c): $(\times 3) (\times 5/8)$

Photo. 2. The morphology of solidification interface for carbon steel ingot $(\times 3) (\times 5/8)$

maining liquid which had been clinging to the dendritic aggregates. Photographs 1 (b) and (c) show clearly the solidification interface with pyramidal protrusions in larger magnification. Photograph 2 represents the solidification interface with pyramidal protrusions in a steel ingot. It is clearly shown that the solidification interface has the solidifying zone and also the pyramidal protrusions, which are composed of dendritic aggregates in a regular fashion, in steel as well as in Al-Cu alloy.

It is also necessary to obtain experimentally the value of the critical fraction of solid, Sp , above which the liquid is completely entrapped by the solid. Photographic observations were made on the dendrite structure of the vertical sections 3, 5, and 8 mm apart from the mold in the columnar zone of a S45C carbon steel ingot of 800 g in weight and 30 mm in dia. The distance between the dendrites and the total area of dendrites per unit area were measured in the present investigation. Finally schematic dendrite morphologies were drawn on the basis of the photographic observations. An example of the results obtained is shown in Fig. 6. As the results, Sp was decreased from 69 to 65% with the increase of the distance from the chill. This value agrees well with the value of Sp calculated for Al-Cu alloy, 67%, as described above. Recently, Tsuda *et al.* reported that the value of Sp is in the range of 53 to 61% for carbon steels of 120 kg.³¹⁾

2. Effective Distribution Coefficient for Steel

Mitsuo *et al.* reported that the flow velocity of free convection is 0.5–10 cm/sec by Wojcik, 0.17–1.7 cm/sec by Mori, and 2.6 cm/sec by Romanov, respectively, for the killed steel ingots.³²⁾ Using Eq. (5-a) and $U = 10$ cm/sec which is the maximum flow velocity of free convection, the value of the effective distribution coefficient is estimated to be more than 0.93 for the killed steel ingot. It is thus evident that the solidifying zone is not washed so much by the free convection of bulk liquid in the case of killed steel ingot. How-

ever, it is expected that the effective distribution coefficients of phosphorous and sulphur are increased over unity at the top of the ingot and decreased below

Fig. 6. Photographs showing the dendrite structure for carbon steel at the fractions of solid 68 and 63% ((a)-(d)) and schematic illustrations of the dendrite morphology ((e) and (f))

(a) and (b): ($\times 40$) ($\times 5/7$)

(c) and (d): ($\times 100$) ($\times 5/7$)

Table 1. The minimum effective distribution coefficients in the rim-zone of rimming ingots

Alloying element	Equilibrium distribution coefficient		Minimum effective distribution coefficient						
	k_0 in $\bar{o}$ -crystallization	Ref.	k^* (Calculated)	k^* (Observed)			Ref.		
C	0.13	(33)	0.42	0.42	(39)				
		(34)		0.42				(34)	
	0.20	(35)		0.46				(5)	
	0.29	(6)		0.52				0.50	(40)
Mn	0.72	(33)	0.81	0.79	0.80	(41)			
	0.76	(36)	0.84	0.85	0.90			0.91	
	0.84	(34)	0.89	0.90	0.91			0.92	(40)
	0.90	(35)	0.93	0.90	0.92			(34)	
P	0.06	(33)	0.37	0.38	0.46	(41)			
	0.13	(34)	0.42						
	0.2–0.5	(37)	0.46–0.67					0.63	0.65
S	0.02	(35)	0.34	0.33	0.34	0.37	(44)		
	0.032	(6)	0.35	0.36	(45)				
	0.04	(38)	0.36	0.38	0.39	0.40	(41)		
	0.05	(34)	0.36	0.41	0.42				

0.93 at the bottom of the ingot, since a considerable gravity segregation takes place in the solidifying zone.¹¹⁾ It is thus considered that the macrosegregation in the killed steel ingot is controlled partly by the degree of washing against the solidifying zone with the free convection of bulk liquid and partly by the gravity segregation in the solidifying zone.

If the solidifying zone is completely washed out by the fluid motion of bulk liquid during the solidification of alloy, the liquid between dendrites shows the same concentration as the bulk liquid when the fraction of solid is decreased below 67%, *i.e.* in the q zone. The solute concentration of bulk liquid may increase in the later stage of solidification. But it can be assumed to be the same as the initial solute concentration of the liquid in the early stage of solidification. Then the minimum effective distribution coefficients of carbon, manganese, phosphorous, and sulphur in the steel ingot are calculated by inserting the same critical fraction of solid as obtained for Al-Cu alloy, 67% and their equilibrium distribution coefficients into Eq. (9). Table 1 shows the calculated and observed values of the minimum effective distribution coefficients. Table 1 clearly shows that these calculated values are approximately equal to the minimum effective distribution coefficients observed for the rim-zone of rimming ingots. It is found that the macrosegregation in the rim-zone of rimmed steel ingot is determined only by the degree of washing against the solidifying zone with the turbulent flow of bulk liquid.

IV. Conclusion

In order to understand the solidification phenomena of steel ingots, it is most important to clarify the behaviour of the solute-rich liquid which is formed between dendrites in the region of partial solidification, *i.e.* the solidifying zone. Accordingly, the segregation behaviour and the solidification mechanism were theoretically examined on the basis of a model experiment, in which the morphology of dendritic growth and the fluid flow of bulk liquid during the solidification of Al-4wt%Cu alloy were studied. The results obtained are summarized as follows:

The effective distribution coefficient, k^* , is represented by

$$k^* = 1 - EU$$

where E is an experimental constant and U is the flow velocity of bulk liquid. Thus k^* depends only on U . However, there is a minimum in the value of k^* . The minimum effective distribution coefficient, k_m^* , is expressed by

$$k_m^* = 1 - Sp(1 - k_o)$$

where Sp is the critical fraction of solid above which the liquid is completely entrapped by the solid and k_o is the equilibrium distribution coefficient. Since the value of k_m^* is 0.45 for Al-4wt%Cu alloy, the value of Sp is calculated to be 67%. This agrees well with the value of Sp actually observed for carbon steel, 65 to 69%. Assuming that the value of Sp is equal to

0.67, the minimum effective distribution coefficients calculated for the alloying elements in steel are obtained as follows: 0.42 for carbon, 0.81 for manganese, 0.37 for phosphorous, and 0.34 for sulphur respectively. These values agree well with the minimum effective distribution coefficients observed for the rim-zone of rimming ingots. From these, it is evident, that the macrosegregation in the rim-zone of rimmed steel ingot is determined only by the degree of washing against the solidifying zone with the turbulent flow of bulk liquid.

List of Symbols

a :	slope of the liquidus line on the phase diagram
A :	turbulent diffusivity
A_D :	turbulent diffusivity of mass
A_r :	turbulent diffusivity of momentum
b :	distance between columnar crystals
B :	constant determined on the basis of hydrodynamics
c :	specific heat of the q zone
C_{Lo} :	initial solute concentration of the liquid
$\bar{C}_p$:	average solute concentration of the p zone
$\bar{C}_s$:	average solute concentration of the solid zone
D :	diffusion coefficient of the solute
E :	empirical constant
F :	solidifying zone which is composed of solid and liquid phases
G :	temperature gradient
h :	thickness of the q_1 zone
j :	effective cross section for diffusion
k_o :	equilibrium distribution coefficient
k_o' :	nonequilibrium distribution coefficient
k^* :	effective distribution coefficient
k_m^* :	minimum effective distribution coefficient
L :	latent heat of fusion
$(\dot{m})_{x=h}$:	quantity of the solute which is transported per unit time outside of the q_1 zone by turbulent mixing at $x=h$
p :	zone in which the liquid is entrapped by the solid
q_1 :	zone in which the solid forms dendrite skeleton and the liquid can flow through the dendrite arm spacings
q_2 :	zone in which the solid as well as the liquid can flow
Q :	mass (or momentum) which is transported per unit time by turbulent mixing
r :	distance from the center of the inner cylinder to the fluid
r_o :	radius of the inner cylinder
Sp :	critical fraction of the solid above which the q zone changes to the p zone
T_a :	tapping temperature
T_E :	equilibrium liquidus temperature
T_s :	equilibrium solidus temperature
T'_s :	virtual solidus temperature
$T'(x)$:	temperature profile of the q zone
$T_L(x)$:	temperature profile of the bulk liquid
U :	flow velocity of the bulk liquid

U_s : peripheral velocity of the inner cylinder
 V : rate of solidification
 W : mass (or momentum) which is transported by turbulent mixing
 x : distance from the boundary between the p and the q_1 zones to the tip of q_1 zone
 α : thermal diffusivity of the bulk liquid
 α' : thermal diffusivity of the q zone
 δ : thickness of the diffusion layer at the planar interface
 δ_l : thickness of the laminar sub-layer
 δS : fraction of the solid which is initially formed when undercooled by δT_c
 δT_c : degree of undercooling
 δh : thickness of the mixing zone in the q_1 zone
 ρ : density of the q zone
 λ : heat conductivity of the q zone
 μ : viscosity
 ν : kinematic viscosity
 τ : shearing stress

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