On Formation Mechanism of Negative Segregation Zone (alias “Settling Crystal Zone”) of Large Steel Ingots*

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Synopsis

Proposed theories on the formation mechanism of the negative segregation zone in large steel ingots seem still unsatisfactory due to lack of direct investigation on the formation process.

The author carried out a series of experiments (i.e., bar-test, sampling, and temperature measurement) on 3-t steel ingots solidified in sand moulds to investigate directly various phenomena taking place during the solidification process.

As a result, it was shown that the negative segregation could be explained by an entirely different formation mechanism from the usual theories proposed in literatures. The author's new interpretation is based on the following three experimental results.

- (1) *Decrease of the solidification rate in the negative segregation zone and decrease of the effective distribution coefficient due to the decrease of the rate,*
- (2) *wide range solidification zone in the negative segregated zone, and*
- (3) *rising of segregated molten steel.*

I. Introduction

Generally, there is negatively or inversely segregated zone, so-called settling crystal zone, in the lower central part of large ingots, where macroscopic oxide inclusions and sand inclusions are frequently observed.

There seems some relation between inclusion distribution and the inverse segregation.

On the other hand, these oxide inclusions are one of the fatal faults of ingot quality. Since a long time ago, many efforts have been made to clarify the cause of these faults and to decrease the inclusions.

Many interpretations have been presented and discussed on the inverse segregation and the inclusions. Among them, the so-called “settling crystal theory” based on the settling action of crystals is still supported by many investigators.

However, this theory started without confirming the actual settling phenomenon of crystals, but assumed this phenomenon from the observation of the inner structure of steel ingots at room temperature. So this theory lacks an actual proof.

The author tried to clarify this problem and eventually to improve ingot quality.

First of all, formation mechanism of negative segregation zone was studied and the settling crystal theory was re-examined. Then, the present results showed that this theory is not reasonable to explain formation mechanism of negative segregation zone. Also from the results of many experiments and discussions it was found that this segregation might be explained by another mechanism different from the settling crystal theory.

The author gives the outline of a new formation

mechanism of negative segregation zone, with discussion on the controversial points of the settling crystal theory.

II. Weak Points of Generally Accepted Formation Mechanism of Negative Segregated Zone

The oldest proposal for the formation mechanism of negative segregation zone is the so-called settling crystal theory by Heterogeneity Committee of Iron and Steel Institute of U. K.¹⁾

This theory states that at optional points of molten steel high purity crystals nucleate and grow, which have larger density than the melt around them. So pure crystals fall down in the melt and are accumulated at the lower portion of a steel ingot, resulting in the negative segregation zone.

However, from examination on falling rate of crystals in this explanation, there rose many objections to the statement that crystals nucleate at optional points of melt.

The Committee²⁾ re-examined this explanation and corrected by saying that the main cause is the floating-up of segregated melt from the lower part of ingot to the upper part rather than the falling down of high pure crystals.

The Heterogeneity Committee confirmed the settling phenomenon of crystals and explained the formation of the negative segregation zone only by considering the counter movement of crystals and the melt due to density difference.

However, this theory still holds many unsolved questions. First of all, there is no definite answer for the question, whether or not random nucleation in melt can produce enough precipitation to form the negative segregation zone. Second, if the precipitation of crystals is the main cause for the formation of the negative segregation zone, the precipitated crystals will be purer at the nearer part to the bottom of ingots where melt solidifies at first. Therefore, the concentration of each solute elements should be the lowest in this part. However, as observed usually on large steel ingots, the centre of the negative segregation zone where the concentration of each solute elements are the lowest, has been found at the one third from the bottom of ingots. This position differs from the centre estimated from the settling crystal theory.

The more it approaches to its centre, the lower become these concentrations. Such contradictions to the settling crystal theory might be caused by the attempts to explain the formation of the negative

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segregation zone only by the movement of matters.

Northcott,³⁾ Melting and Metallurgical Committee of Iron and Steel Institute of U.K.,⁴⁾ West,⁵⁾ Gray⁶⁾ *et al.* made experiments using horizontal ingots, and discussed the results with the settling crystal theory.

They examined the inner structure of ingots and found that under the same heat condition columnar crystals were longer when solidification started from the upper surface of ingot than from the lower surface of ingot. As the reason, in the upper part of ingot crystal particles formed in the vicinity of the solidification front fell down to the bottom, and thus, columnar crystals continued to grow. However, in the lower part of ingot, crystal particles falling down from the upper part were accumulated on the solidification front and suppressed the growth of columnar crystals. From the previous experimental results on the small steel ingots with sand moulds, the author⁷⁾ showed that such a phenomenon could be explained by another interpretation different from the settling crystal theory.

It may be clear that there are many questions remained unsolved in this settling crystal theory. One of the most essential weak points is that this theory was derived only from the experimental results after ingots were completely solidified. The intermediate process of solidification was not experimentally studied.

On the other hand, away from the above-mentioned gravity theory, Benedicks,⁸⁾ Gray,⁶⁾ Kosmider *et al.*,⁹⁾ Mori *et al.*,¹⁰⁾ Cole and Winegard,¹¹⁾ and Iizima and Inamoto¹²⁾ studied the solidification from the side of ingot. From experimental results using models or R. I. and others, it seems that the thermal convection took place due to the temperature gradient of horizontal direction between solidification interface and centre line of ingots. In the vicinity of the front of solidifying interface, this convection formed falling down current. Thus, crystal particles crystallized at the front fell down and dendrites were destroyed. This theory is called the convection theory, which is still based upon the settling phenomenon of crystals.

There are many questions about this theory. First of all, in this theory it is assumed that the effect of convection on the settling phenomenon of crystals is large during the growing period of columnar crystals. However, it is not sure that the degree of supercooling is enough to produce new crystal particles in melt close to the solidification front of columnar crystals.

According to the formation mechanism of columnar crystal and equiaxial crystal, it is presumed that the degree of supercooling is not very large. With the constitutional supercooling branched dendritic crystals are formed at the position where columnar crystals transform to equiaxial crystals, thereafter the formation of equiaxial crystals starts. New crystal particles could not be formed at this position. However, when the branched dendritic crystals really start to take place, convection current vanishes out and "inverse V ghosts" are formed. From these facts, convection during the growth of columnar crystals may not be related to the settling phenomenon of crystals.

Second, even if crystal particles are transported by

the convection, it is very doubtful that the amount of crystal particles carried by convection is enough for formation of the negative segregation zone.

Third, if the negative segregation zone is mainly formed by the settling action of crystals, the concentration of elements should be lowered at nearer points to the centre of the negative segregation zone, because the concentration of columnar crystal zone is generally uniform.

Marburg¹³⁾ denied the existence of settling crystals from the results of pour-out tests on many kinds of ingots and proposed a new theory. It seems that there are many contradictions in his interpretation.

All the above-mentioned theories have many faults to explain the phenomena.

Thus, the author proposes a more reasonable interpretation for the formation mechanism of the negative segregation zone.

III. Experimental Results on 3-t Steel Ingots with Sand Mould

1. Solidification Condition and Inner Structure of 3-t Steel Ingot Cast in Sand Mould

Experimental Method

Plain carbon steel (ladle analysis: C: 0.23%, Si: 0.38%, Mn: 0.70%, P: 0.019%, S: 0.016%) melted in 6-t basic electric arc furnace. The melt was cast at 1535°C in the sand mould by the bottom casting (inner surface temperature: 120°C). The mould is shown in Fig. 1. Temperature of melt was measured by an immersion pyrometer. The feeder head was protected from heat loss by heat-insulator and straw. Melt was deoxidized in ladle by 0.03% Al.

Vertical and transverse solidification rates were measured by means of a simple apparatus.

After solidification, the ingot was cut longitudinally along the centre line, and the segregation of chemical elements, sulphur print and macrostructure were investigated.

Fig. 1. Equi-solidifying line of 3-t steel ingot cast in sand mould

Experimental Results

i. Solidification Rate

Figure 1 shows movement of solidification front obtained from experimental results.

As shown here, the solidification rate is relatively rapid until 0.5 hr after casting, but slow in the period of 0.5 to 3.0 hr. In the period of 3.0 to 4.0 hr the rate becomes again suddenly rapid, but slow in the period of 4.0 to 5.0 hr, and solidification advances again rapidly from 5.0 hr till the end of solidification.

The negative segregation zone corresponds to the region where the growth of solidification layer advanced relatively rapid between 2.0 and 4.0 hr after casting.

Vertical and transverse solidification patterns have a similar tendency on the whole, and the apparent solidification rate of the former is about twice that of the latter.

ii. Inner Structure

The macrostructure of longitudinal cross section from the ingot is shown in Fig. 2. The structure is classified roughly into chill crystal zone, columnar crystal zone, equiaxed crystal zone, and feeder head zone with maximum segregation.

Some "inverse V ghosts" are found stringlike. "Inverse V ghosts" begin in the neighbourhood of columnar crystal end and proceed to the inner region of ingots. The end of columnar crystal is located within 30 (in lower part of ingots) and 50 cm (in middle and upper parts of ingots) from the ingot surface. These ghosts never go beyond the so-called branched dendritic crystal zone.

- A: chilled crystal zone
- B: columnar crystal zone
- C: branched dendritic zone (A ghost appeared zone)
- D: equi-axial crystal zone (V ghost appeared zone)
- E, F: apparent accelerated lines of solidification in equi-axial crystal zone
- G: maximum segregated zone

Fig. 2. Schema of macrostructure of longitudinal cross section from 3-t steel ingot cast in sand mould

On the other hand, "normal V ghosts" are not so clear as "inverse V ghost" and bandlike. "Normal V ghosts" are all found in the equiaxial zone, and thin color zones of sulphur print have been observed by turns with "normal V ghosts".

The negative segregation zone (cf. Fig. 3) is found in the equiaxial zone under the normal V ghost zone, and its centre is located in the position of one third from bottom on the centre line of the ingot.

In this ingot, the equiaxial crystal zone is considerably wide. Thus, the zone is wide for both "normal V ghosts" and negative and columnar crystals of bottom are shorter comparing with that of side.

iii. Segregation of Various Solute Elements

Figure 3 shows the distribution of various elements on the longitudinal cross section from the ingot. It can be seen that the distribution of carbon, sulphur, and phosphorous has a nearly similar tendency.

In the surface layer zone, each concentration is about uniform and nearly equal to that of molten steel at the time of casting. In the lower part of ingot, each concentration decreases with going into the inner part of ingot to form the negative segregation zone (so-called settling crystal zone). The centre of this zone is located at one third on the centre line from the bottom of ingot. At this centre, the concentration becomes lowest. Each concentration is the three fifth of that in the surface layer zone. On the other hand, above this negative segregation zone, each concentration of the inner part is inversely higher than that in the surface layer zone. Such a tendency becomes remarkable with going up to the upper part of the ingot, and the concentration of feeder head region and maximum segregation zone along the centre line of the ingot are 1.5 to 3 times of that in the surface layer zone. The concentration of "inverse and normal V ghosts" zones shows also higher value, and it becomes higher in the order of inverse V, normal V, and maximum segregation zone.

Discussion

As shown in Fig. 2, the solidification structure of the negative segregation zone consists of relatively fine equiaxial crystals. On the other hand, it is thought that in the equiaxial zone the solidification proceeds

Fig. 3. Distribution of various elements in 3-t steel ingot cast in sand mould

dendritically^{15),16)} forming "pasty zone" under the so-called constitutional supercooling condition by Rutter and Chalmers.¹⁴⁾ The growing rate of equiaxial crystals is considered to be controlled by the rate of transfer of the latent heat in the negative segregation zone. Since the negative segregation zone has appeared in the central-axial zone, this heat transfer rate is rapid compared with that in the columnar crystal zone. Consequently, the solidification in the negative segregation zone is generally retarded, and such an effect becomes larger as the front goes into the central part of the ingot and negative segregation rate becomes larger.

Figure 1 shows that the solidification rate in the central part of the negative segregation zone seems to be rapider than that in its circumference. The region where melt solidifies in the period of 3.0 to 4.0 hr after casting is wide, contrary to the above conclusion. This fact may be easily explained by the growing rate of crystals themselves, but not by the rate of increase of thickness of solidified layer. Because of the very wide range of the supercooled zone and of large supercooling in this region it is expected that a great many nuclei of crystals are formed. Thus, the solidification in the entire region is thought to progress rapidly although the growing rate of each crystal is retarded. This is also obvious from the fact that in the central region of the ingot the grain size of equiaxial crystals is finer than that in its circumference.

As an explanation of the formation mechanism of the negatively segregated zone, the settling crystal theory has been supported as stated above. It can be explained also by distribution coefficient that the solute concentration in this region is higher than that in surface layer zone and top. Since the solidification rate is relatively rapid in the surface layer zone, its solute concentration is nearly equal to that of the molten steel at the time of casting. In the negative segregation zone, the solidification rate is relatively slow and the floatation-up of segregated molten steel seems to be done sufficiently as shown from model experimental results⁷⁾ by the author. Therefore, it is assumed that the bulk concentration in this zone should not be so high.

From these facts, the value of the distribution coefficient in the negative segregation zone seems so small that the concentration in the zone must be lower than that in the surface layer zone after solidification.

2. Behaviours of Solute Elements during Solidification Process of 3-t Steel Ingot Cast in Sand Mould

Experimental Method

Plain carbon steel (ladle analysis: C: 0.24%, Si: 0.31%, Mn: 0.61%, P: 0.012%, S: 0.010%) melted in 6-t basic electric arc furnace was cast at the same time into two sand moulds as Fig. 4 by bottom casting at 1540°C (measured by immersion pyrometer). The feeder head was protected from heat loss by heat-insulator and straw.

Samples were simultaneously taken from several positions on the centre line of the ingot (cf. Fig. 4)

at the time of 1, 2, 3, 4, and 4.5 hr after casting. The sampler is shown in Fig. 5. Samples were quenched in water.

No. 1 ingot of two ingots was solidified naturally without stirring, but No. 2 ingot was solidified with stirring treatment for a certain time after casting by blowing argon gas. Table 1 shows the details of this experimental procedure.

Samplers were pre-heated enough to avoid sticking and temperature drop of molten steel, and they were inserted with attention lest slag should stick to them.

After solidification, the ingot was longitudinally cut and behaviours of solute elements during the solidification process were examined by comparison of their concentration before and after solidification.

Experimental Results and Discussion

Figure 6 shows the change of each solute element in the remaining molten steel (except for silicon and manganese). As shown here, all of carbon, sulphur, and phosphorus have a tendency to increase with solidification. Moreover it is found that their enrichment becomes higher in the upper part of ingot. This fact evidently shows that the enrichment of solute atoms in the remaining molten steel takes place accumulatively

Fig. 4. Shape of experimental ingot and sampling locations

Fig. 5. Sampling tube

with the solidification. On the other hand, the solute concentration after solidification becomes the lowest in the so-called negative segregation zone. The all

Table 1. Development of sampling experiment

Time after pouring (hr)	No. 1 ingot Sampling progress	No. 2 ingot		Remarks
		Ar gas blowing progress	Sampling progress	
1.00	5 min		A.B.C.D.E	Because of gauge accident, Ar gas blowing amount and blowing pressure are indistinct.
2.00	6 min	7 min	A.B.C.D	
3.00	6 min	15 min	6 min	
4.00		1 min	A.B.C	A : 80 mm below from fixed location A B : 600 mm over from bottom surface A : 200 mm below from fixed location A
5.00			6 min	
			A.B	
			A	
			3 min

Fig. 6. Concentrating conditions of various elements during solidification process

solute concentrations in this region have already become higher before solidification than that of the molten steel (initial concentration) at the time of casting.

Such a phenomenon contradicts evidently the so-called settling crystal theory which has been asserted so far. According to this theory, the solute concentration before solidification at the position corresponding to the negatively segregated zone must be lower than that of initial molten steel. The composition of the melt must be of close value to the concentration after solidification, because the high purity crystals precipitate in the region above the negative segregation zone in the early period of solidification. Thus this theory contradicts evidently this experimental results. But the density of high purity crystals is somewhat larger than that of molten steel and it seems impossible to deny entirely the falling phenomena of these crystals. It is proper to consider that such a settling action of crystals should not play a major role in the formation of the negative segregation zone.

How the negative segregation zone is formed under the present conditions? For simplicity Fe-X binary system is considered below.

Figure 7 shows the equilibrium phase diagram of binary iron alloy in the neighbourhood of its melting point. In this diagram, if the molten steel with the concentration of solute element X, or $C_x^{L(o)}$ is cast and equilibrium solidification takes place, the concentration of surface layer zone solidified first is given as K_x^* , $C_x^{L(o)}$, where K_x^* means equilibrium distribution coefficient. If the solidification proceeds to the inner part of ingot with the enrichment of solute element, the concentration of molten steel increases along the liquidus. The solidification rate in the surface layer zone is considerably rapid and equilibrium solidification does not take place. The concentration of the solid becomes a function of solidification rate as reported by Burton *et al.*¹⁷⁾ and becomes fairly a close value to the concentration of molten steel at the time of casting, or $C_x^{L(o)}$, depending on the following equation.

$$C_x^S = \frac{C_x^{L(o)} K_x^*}{K_x^* + (1 - K_x^*) \exp -u\delta/D_x} \quad \dots\dots\dots (1)$$

where, C_x^S : concentration after solidification
 δ : thickness of diffusion layer
 D_x : diffusion coefficient
 u : solidification rate.

As noted above, the solidification rate in the negative segregation zone is expected to be considerably slow. Thus, it may be concluded that the solidification proceeds nearly in equilibrium state. If the solute concentration just before solidification in this region is less than $C_x^{L(o)}/K_x^*$ (according to (1) the concentration is practically, lower than this value because of the finite solidification rate), the concentration after solidification must be lower than that of initial molten steel. Besides, in this region the solidification rate is considerably slow and segregated molten steel rises up rapidly, so that the concentration in bulk melt cannot be very high. Hence, the above tendency may become clearly notable.

The same behaviour is expected reasonably in the upper region of the negative segregation zone. Before solidifying in this region, bulk concentration must be high, since the segregated molten steel has risen up fast from the bottom. As a result, the concentration after solidification should become equal to or higher than that in the surface layer zone, producing the positive segregation.

As examples of segregation before and after solidification, carbon and sulphur content in the central-axial region is presented in Fig. 8. As seen in Fig. 8, in the central-axial region of ingot, the negative segregation zone is found to cover a wide range from bottom

Fig. 7. Phase diagram of iron near melting point

Fig. 8. Segregation of carbon and sulphur before and after solidification for No. 1 ingot

end up to about 60 cm, and the center of this zone is located at about 30 cm from bottom end. The segregation is found similarly for other elements. All concentration curves show a tendency to increase and then to become flat at the upper limit of the negative segregation zone. As noted above, the solidification at this position proceeds in a similar way to that in the negative segregation zone. The shape of the curves in Fig. 8 are affected by the fact that in this part the solidification takes place in a relatively wide range and the solidification within that range is completed at about the same time. This, as shown in Fig. 1, is indicated by the fact that the solidification proceeds stepwise in this part. However, when the solidification in this part takes place, the bulk concentration is higher than that when the negative segregation zone is formed and so the concentration of the solid shows positive segregation.

As shown in Fig. 6, the concentration gradient has already been formed from bottom to top in the bulk melt one hour after casting and this gradient increases with time.

This suggests that the segregated molten steel on the solidification interface floated upward at relatively rapid rate. Assuming from the model experimental results of the author, this floatation-up mechanism is supported by the fact that specific gravity of the segregated molten steel is smaller than that of bulk melt. The stirring action may accelerate rising the enriched melt.

On the other hand, temperature measurement during solidification process showed that the temperature in the negative segregation zone became higher than that in the upper region of its zone. Thus, it is expected that the thermal convection takes place in bulk. If the thermal convection takes place not so strongly as to make the bulk concentration uniform, rising of the segregated molten steel would be accelerated. If so, the concentration gradient in bulk should be developed much more.

This fact is indicated clearly by comparison of the concentration distribution of No. 1 ingot with that of No. 2 ingot one and two hours after casting. Both concentration distributions are nearly equal, but the degree of segregation and concentration gradient in No. 2 ingot with stirring two hours after are both larger than those in No. 1 ingot without stirring.

This segregation in bulk melt and the formation of concentration gradient during solidification process cannot be explained without the consideration of dynamic mass transfer.

3. Temperature Measurement during Solidification Process of 3-t Steel Ingot Cast in Sand Mould

It is necessary for the study of the formation mechanism of the negative segregation zone not only to investigate the behaviour of solute atoms during the solidification process of steel ingot but also to clarify the solidification mechanism. The temperature in the central-axial part of ingot was continuously measured during solidification process using 3-t steel

ingot. From these results, the formation mechanism of the negative segregation zone was considered.

Experimental Method

In the sand mould, same as shown above, 0.5 mm dia. Pt-Pt-Rh thermocouples were previously set at several positions as shown in Fig. 9. A most reliable protecting method of the thermocouple was selected as in Fig. 10 from various preliminary experiments.

Plain carbon steel (ladle analysis: C: 0.25%, Si: 0.38%, Mn: 0.69%, P: 0.018%, S: 0.014%) melted in 6-t basic electric arc furnace was cast in the above-mentioned mould at 1535°C (measuring by immersion pyrometer) by the bottom casting. Feeder head was protected from heat loss by heat-insulator and straw.

The temperature was continuously measured until the completion of solidification.

Experimental Results and Discussion

The measurement at the position of C_2 in Fig. 9 was impossible because of the breakdown of the protection tube at the time of casting, but the measurement at all the other positions were carried out until the completion of solidification. Figure 11 shows the results.

i. Retardation of Solidification in Negative Segregation Zone

In Fig. 11, No. 4 curve corresponds to the tem-

Fig. 9. Form of sand mould and measuring positions

Fig. 10. Protecting tube of thermocouple

perature change at the centre of the negative segregation zone. Temperature at the central part of the negative segregation zone drops to 1500°C about one hour after casting, and hereafter is constant lasting for about two hours. This constant value for long hours may be caused by the peritectic solidification (in the Fe-C system, it is between 0.07 to 0.36%C at 1480°C), because the carbon content in this part just before solidification is assumed to be about 0.30%. Thus, the solidification might already have begun in this part at least one hour after casting. It is presumed that the solidification in the central part of the negative segregation zone starts at comparatively early period. Hereafter the temperature drops gradually and the solidification is completed near 1450°C about 50 min later. Duration between the start and the end of solidification is over three hours or considerably long hours. This solidification duration as shown in Fig. 1 is by far longer than that in the columnar zone, where the solidification finished about 30 min after casting. This fact seems to prove sufficiently the retardation of solidification in the negative segregation zone, as previously pointed out.

This retardation of solidification may be caused by the latent heat released when each equiaxial crystal grows dendritically with slow heat transfer. The solidification rate of each equiaxial crystals becomes naturally slower too, corresponding to the length of solidification duration. As a result, it is sufficiently conceivable that the effective distribution coefficient in the negative segregation zone becomes smaller than that in the surface layer zone and the concentration of elements in this zone becomes less than that in the surface zone.

ii. Wide Range Solidification in Negative Segregation Zone

The solidification is discussed in the region where a negative segregation degree is comparatively low within the negative segregation zone.

In Fig. 11, No. 5 curve shows the temperature change at the position under the central part of the negative segregation zone. As shown in this part the temperature drops to 1480°C about 30 min after casting, hereafter a little higher temperature lasts for 1 hr 45 min, and begins to drop again. 30 min later the solidification is completed at about 1450°C.

From No. 3 curve of the temperature change at the

Fig. 11. Result of measuring temperature during solidification process in 3-t steel ingot cast in sand mould

position over the central part of the negative segregation zone, it is found that in this part the temperature drops to 1 490°C about 1 hr 45 min after casting, lasting for about 2 hr 15 min, then the temperature begins to drop again and 1 hr 10 min later the solidification is concluded at about 1 430°C.

Comparing the results of these three cases, it is found that the time of solidification starting becomes later from lower part to upper part and the end of solidification is also in similar order. Such a phenomenon should be easily expected from heat transfer rate of the latent heat of solidification in each position. As shown in Fig. 12, there is a period when the solidification is simultaneously proceeding at three positions extending over one hour from about 1 hr 45 min after casting. This fact shows that the solidification in the negative segregation zone has proceeded over a comparatively wide range. Thus, in this region, a very viscous zone is widely formed.

iii. Solidification in Positive Segregation Zone of Central-Axial Part

In the positive segregation zone, which is situated over the negative segregation zone, temperature changes as No. 1 and No. 2 curves in Fig. 11. The solidification begins two hours after casting. Hereafter the temperature drops gradually without a constant value as that in the negative segregation zone, then the solidification is completed at 1 320°C for No. 1 and at 1 300°C for No. 2 about 4 hr 30 min after the beginning of solidification.

Because the peritectic solidification does not take place in this part, it may be assumed that the bulk is considerably concentrated. Such an assumption agrees with the above-stated sampling results.

The temperature in this region is always lower than that in the negative segregation zone through the process of solidification. This phenomenon has never been recognized because of lacking the continuous temperature measurement during solidification process. This measurement contradicts the usual estimation that temperature at the upper part is always higher than that at the lower part in ingot.

The reasons for this temperature distribution will be clarified in the future and the details can not be discussed in this paper, except the following two factors.

(1) The starting time of solidification in the negative segregation zone is earlier than that in the

positive segregation zone.

(2) Bulk melt concentration at the starting time of solidification is lower in the negative segregation zone than in the positive segregation zone.

That is to say, in the positive segregation zone, the bulk melt concentration gradually increases because of rising of segregated molten steel, affecting lowering of the solidification temperature. Only heat transfer takes place and the temperature keeps on lowering. In the negative segregation zone, the solidification begins earlier than in the positive segregation zone. The concentration in the negative segregation zone at the solidification beginning is lower than that in the positive segregation zone. The temperature at which the solidification begins is high and the transfer of the latent heat of solidification takes place. As a result, the state of higher temperature lasts in the negative segregation zone rather than in the positive segregation zone. Once the solidification is completed in the negative segregation zone, only the heat is transferred into this zone. In the positive segregation zone, the melt still continues to solidify and the temperature in the positive segregation zone becomes higher than that in the negative segregation zone.

iv. Solidification Period and Segregation Phenomenon at Each Position of Central-Axial Region

As shown in Fig. 12, the time of solidification beginning and completion, and solidification period become late and long respectively, from the lower part to the upper part in the ingot. These phenomena are naturally based on the condition of heat transfer at each position. However, this is mainly caused by the concentration gradient formed in the bulk with rising of the segregated molten steel from the lower part to the upper part during the solidification process. Consequently, liquidus and solidus temperatures drop in the upper part. Figure 13 shows solidification beginning temperature (liquidus temperature) and solidification completing temperature (solidus temperature) at each position of this ingot. Considering the Fe-C binary system for simplicity and using these values, the following carbon contents were calculated in the molten steel at each position at the time of solidification beginning.

	No. 1	No. 2	No. 3	No. 4	No. 5
C (%)	0.75	0.60	0.33	0.30	0.28

Fig. 12. Solidifying period at each location of centre-line part of 3-t steel ingot cast in sand mould

Fig. 13. Liquidus and solidus at each locations of centre-line part of 3-t steel ingot cast in sand mould

These values agree approximately with the results of chemical analysis of samples. From these facts, it is safely expected that the decrease of solidification point happens with rising of segregated molten steel during solidification process. On the other hand, the time of the solidification completion at each position shows a good agreement with the results of the bar-test mentioned above.

IV. Formation Mechanism of Negative Segregation Zone

From the above-mentioned results, a new interpretation was obtained for the formation mechanism of the negative segregation zone. It was confirmed from temperature measurement that the solidification in the negative segregation zone is retarded in comparison with that in its surrounding zone.

This retardation of solidification may be due to the fact that the transport rate of the latent heat of solidification is small, while each equi-axial crystal grows dendritically. The solidification rate of each equi-axial crystal becomes naturally small according to the time necessary for the completion of solidification. Such a tendency is distinctest in the central region.

On the other hand, it was found from experimental results on the growing rate of solidification layer by bar-test and temperature measurement that the solidification in the negative segregation zone takes place to a certain extent. A few hours are necessary for the formation of this zone. The solutes are enriched in this zone to a certain extent. Because the temperature gradient in the vicinity of the solidification interface has also decreased already, the constitutional supercooling should extend over a comparatively wide range and its degree must be considerably large. In this region many crystal nuclei are formed according to the degree of supercooling and continuously those dendritic growth takes place, resulting in the formation of the pasty zone where both of liquid and solid exist in mechanically mixed state.

From the retardation of solidification over a wide range, it is expected that many crystal nuclei are formed in the negative segregation zone and they grow very slowly. But, because there are many crystal nuclei, the growth of each nucleus has its limits. The size of crystal grains found in the negative segregation zone is generally finer than that in other zones.

If fine crystal nuclei grow slowly and the bulk concentration is not very high, the effective distribution coefficient of each crystal grain becomes lower than that in the surface layer zone where solidification rate is rapid. Hence, it must be expected that the solute concentration in the negative segregation zone becomes less than that in the surface layer zone.

From the sample analysis during solidification process and from the model experiments⁷⁾ it was found that the rising rate of segregated molten steel is comparatively large and the concentration gradient is formed in bulk melt. Therefore, it should be expected that the bulk melt concentration in the negative segregation zone becomes little higher than that at the time

of casting, but it is not so high as to form the positive segregation.

As stated above, formation mechanism of the negative segregation zone could be explained by an entirely different interpretation from usual ones, if following three points are considered:

1. retardation of the solidification in the negative segregation zone and decreasing of the effective distribution coefficient,
2. wide range solidification in the negative segregation zone, and
3. rising of segregated molten steel.

V. Summary

The formation mechanism of the negative segregation zone in large steel ingots have been interpreted by many workers but these conventional interpretations are not satisfactory.

A series of experimental results about 3-t steel ingots have shown that the mechanism could be explained by the entirely different way from usual interpretations. The author's new interpretation is based on the following three experimental observations:

1. retardation of the solidification in the negative segregation zone and decreasing of the effective distribution coefficient,
2. wide range solidification in the negative segregation zone, and
3. rising of segregated molten steel.

However, further studies are necessary to conclude this interpretation.

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