

SOLIDIFICATION OF STEEL INGOTS

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INTRODUCTION

The central aim of this paper is to explain the solidification process and the control of the solidified structure of steel ingots using the newly proposed theory of the formation of an equiaxed zone, the so-called "Separation theory".

To control the solidified structure of steel ingots, it is most important to know the principal mechanism of the formation of equiaxed crystals of cast steels, and then to find factors which influence the formation of equiaxed crystals and suitable controlling techniques of the solidified structure.

Based on the direct observation of the solidification phenomenon of tinbismuth alloys, the author proposed a new theory. That is that the principal mechanism of the formation of equiaxed crystals is the separation of neck-shaped crystals from the mould wall in the initial stage of solidification before the formation of a stable solid skin.

In this paper, first the formation of equiaxed crystals will be discussed and then the solidification process of steel ingots will be discussed based on the new theory of the formation of an equiaxed zone of cast metals.

Lastly, the formation and elimination of macrosegregation in steel ingots the formation and prevention of hot bearing during solidification will be discussed.

THE FORMATION OF EQUIAXED CRYSTALS

The equiaxed chill zone has been believed to consist of five crystals which were formed by "copious nucleation" in the undercooled zone in the liquid near the mould wall (1). However, it was pointed out that the copious nucleation mechanism is not responsible for the formation of the equiaxed chill zone and that

presence of convection plays a decisive role in the formation of the equiaxed chill zone (2,3).

Several theories (4-7) have been proposed on the formation of the central equiaxed zone of cast metals. However, none of the theories proposed on the formation of equiaxed crystals can explain by itself all the solidification problems, such as, the existence of equiaxed crystals both in the outer chill zone and the central zone of an ingot, the formation process of negative segregation and abnormal coarse grains in steel castings.

The present author and his coworkers (8,9) observed the solidification phenomenon of high purity tin and tinbismuth alloys, and proposed a theory based on the results that the formation of equiaxed crystals is due to the separation of neck-shaped crystals from the mould wall at the initial stage of the solidification before the formation of a stable solid skin. This theory was supported by further studies of ammonium chloride-water model (10), of castings of aluminium alloys (11) and of some eutectic system alloys (12).

Based on this theory, the author believes that, to get a fine equiaxed structure, a metal must contain a solute which segregates during the solidification to form neck-shaped crystals on the mould wall; that the formation of a stable solid skin must be prevented; that the separation of crystals should be promoted by dynamic motion in the liquid; and lastly, that pouring temperature of a molten metal must be as low as possible to prevent remelting of the free crystals into the liquid (13).

Previously Proposed Theories:

i) Winegard and Chalmers (4) proposed a theory that the equiaxed zone forms after some initial columnar growth when constitutional undercooling ahead

of growing crystals becomes sufficient for heterogeneous nucleation.

An experiment showed that equiaxed crystals precipitated along the mould wall but were not produced by heterogeneous nucleation ahead of columnar grains in the case of aluminium castings (14). The alloy was melted in a crucible in which a stainless steel gauze was horizontally placed to separate the crucible into two regions, upper and lower, and then the crucible was cooled from outside with water. The resulting ingot structure showed that the equiaxed zone only existed on the gauze although large columnar crystals existed under the gauze. The experiment also indicated that motion of liquid plays an important role for the formation of equiaxed crystals (15).

ii) Chalmers (5), recognizing the inadequacies of his earlier theory proposed what became known as the "free chill crystals theory" or "big bang mechanism". This proposal is that nuclei for equiaxed crystals were formed during the initial chill near the mould wall. These nuclei drifted into the central zone to become equiaxed crystals. He (16) explained that when the metal enters the mould, which is far below its melting point, a layer of metal that is in contact with the mould wall is chilled to such a degree that "copious nucleation" takes place in it. The number of nuclei formed during the initial chill depends upon the effectiveness of nucleant particles, the rate of heat extraction, and the volume of the chilled liquid. If the temperature of the liquid is below what

is required for nucleation, then nucleation takes place throughout the melt.

These two theories are both based on the heterogeneous nucleation of crystals in the undercooled liquid. Therefore, it is impossible to explain by these theories experimental results which were reported by Tarshis and his coworkers (17). They studied the dependence of grain size on undercooling for nickel-copper alloys, and found that, in the lower range of undercooling smaller than 85°C and in the upper range greater than 150°C, the structure was fine and equiaxed, but that the structure was coarse and dendritic in the range between 85-150°C as is shown in Figure 1. The same phenomenon was observed in copper alloys (18), and tin alloys (19).

Since above two theories expect that, when the degree of undercooling increases, the number of crystals which nucleate in the liquid increases, forming finer equiaxed crystals, they cannot explain the increase of grain size which is not inversely proportional to the degree of undercooling as can be seen in Figure 1.

It has been said that some non-metallic compounds act as the nucleation catalysts for equiaxed crystals of steels. For instance, Turnbull and his coworkers (20) reported that the addition of titanium carbide was effective as the grain refiner of steel castings. However, there is no evidence that titanium carbide worked as the heterogeneous nucleant. A recent work (12) on the solidification of eutectic system alloys showed that primary crys-

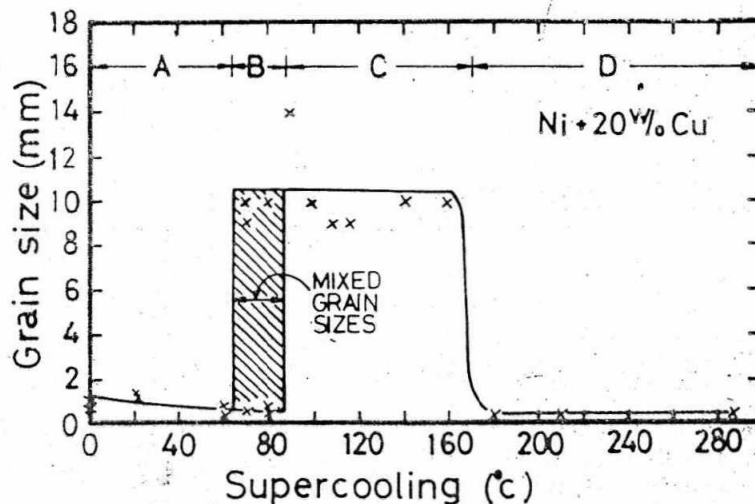


Fig.1 Experimentally determined dependence of grain size on supercooling for nickel-20% copper alloy (from Tarshis, Ref.17)

tals which are the leading phase of the system were the origin of equiaxed eutectic grains while primary crystals of the secondary phase never showed a tendency to be the origin of equiaxed eutectic grains. This suggests that iron particles can work as nuclei of crystals of the central equiaxed zone of steel ingots but nonmetallic particles cannot be nucleation catalysts even when there is a large degree of undercooling. If there is large degree of undercooling at the surface of a non-metallic particle in the liquid, existing primary crystals will preferentially grow into the undercooled region rather than to form nuclei of equiaxed crystals.

iii) Jackson and his coworkers (6) explained that the principal mechanism for the formation of equiaxed zone of ingots is crystal multiplication by melting of arms of growing dendrites.

The detachment of the dendrite arms can occur if the dendrite arms, each having a necked-shape, solidify under an extremely large degree of undercooling, for instance, over 150°C in the case of solidification of nickel-copper alloys (17) and over 20°C in the case of a tin-4% bismuth alloy (19). However, in usual commercial practice, undercooling observed before solidification begins, is rarely more than few degrees centigrade (21).

The remelting of dendrites can also occur when an alloy with a large solidification range is slowly cooled to allow dendrite coarsening. However, this cannot be the principal mechanism of the formation of equiaxed zone of castings because we can often observe ingot structure in which the central equiaxed zone is surrounded by columnar zones which consist entirely of cellular structures but not of dendrites with arms to be separated during the solidification.

iv) Southin (7) considered that the nuclei for equiaxed crystals formed on the free surface of the ingot, and that they then showered down into the liquid ahead of the columnar zone.

Observation on the solidification phenomenon of an ammonium chloride-water model showed that the precipitation of crystals did not occur from the top surface at the stage of crystal growth along the top surface to form a solid skin. Only when the top skin was mechanically destroyed, showering of crystals occurred from the top (10). This phenomenon was

also observed in aluminium testings (10,22).

Showering from the free surface may occur when crystals are prevented from forming a stable top skin, resulting in granular-shape crystals on the top surface. In practice, however, since the precipitation of crystals mostly occur from the upper part of the mould wall before the formation of the stable solid skin, the showering of crystals from the top surface after the formation of the columnar zone cannot be the principal cause of the formation of central equiaxed zone.

Principal Mechanism:

The principal mechanism of the formation of equiaxed crystals should be one which can explain the formation of equiaxed crystals in all cases, even those in the central equiaxed zone which is surrounded by the columnar zone of only cellular structures, even those which were obtained under an extremely small degree of undercooling such as under 1°C, and even those which exist in the outer region of the columnar zone.

To know the principal mechanism of the formation of equiaxed crystals of cast metals, the solidification phenomenon of high purity tin and tin-bismuth alloys were directly observed (8,9). In the case of high purity tin, crystals on the cooling wall first grew along the wall to form a stable solid skin and then grew forward as is schematically shown in Figure 2. The advancing interface of solid and liquid was smooth and flat. The interface gradually grew irregular as bismuth content increased up to 0.5%. However, as the bismuth content was further increased over 1%, an entirely different type of solidification phenomenon was observed. Free crystals which were separated from the mould wall moved toward the hotter side of the liquid. The crystals nucleated on the mould wall first grew, each forming a necked shape, and then separated from the mould wall as is schematically shown in Figure 3. When convection decreased the separation of necked-shape crystals from the mould wall stopped and crystals started to form a stable solid skin which finally became the columnar zone.

The formation of the stable solid skin was promoted by increase of the degree of undercooling. When the degree of undercooling was smaller than 1°C, the separation of necked-shape crystals was

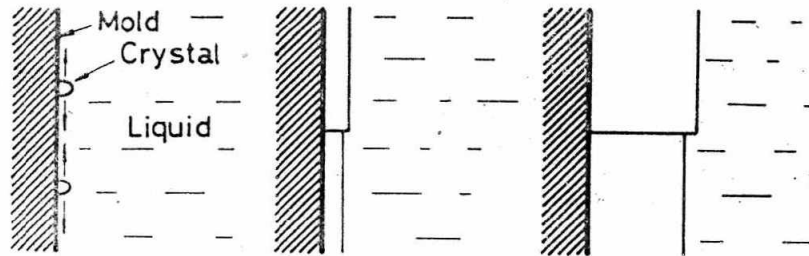


Fig. 2 Schematic illustration of the formation of a stable solid skin.

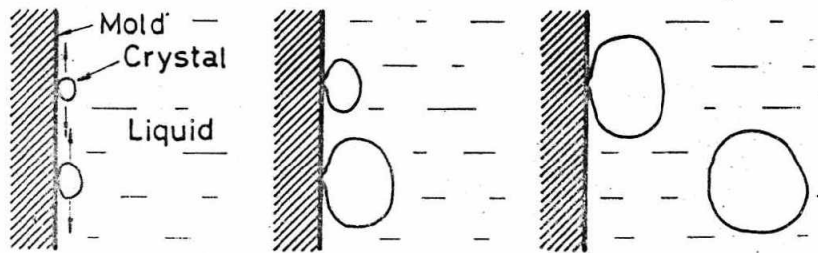


Fig. 3 Schematic illustration of the formation of equiaxed crystals.

observed in the case of tin-4% bismuth alloys. However, when the degree of undercooling was increased to 10°C, the separation of crystals suddenly stopped and columnar crystals started to form on the cooling wall. And when the degree of undercooling was further increased over 20°C, remelting of dendrites was observed, forming fine segments.

Based on this observation, a new theory "Separation Theory" was proposed that the principal mechanism of the formation of equiaxed crystals is the separation of necked-shape crystals from the mould wall at the initial stage of the solidification before the formation of a stable solid skin.

There is other evidence which supports this theory (23). To know the relation between the thermal behaviour at the mould/metal interface and equiaxed zone in the resulting castings, 99.8% Al was poured into moulds made of various materials.

There were two types of heat transfer behaviour at the mould/metal interface, as schematically shown in Figure 4. When the heat transfer coefficient rapidly decreased as shown in Figure 4(a), the resulting structures were only columnar. However, in the case of castings which had an equiaxed zone in the resulting structure, the heat transfer coefficient always showed a tendency to first increase in the initial stage of solidification as shown in Figure 4(b), indicating a delay in the formation of a stable solid skin.

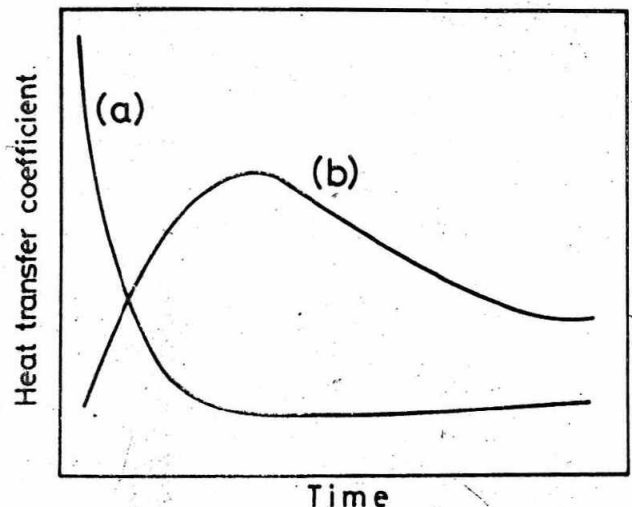


Fig. 4 Heat transfer behavior at the mould/metal interface.

This delay indicates that there is a separation of crystals from the mould wall in the initial stage of solidification.

ORIGIN OF EQUIAXED CRYSTALS

Place where the separation of neck-shaped primary crystals of steels is most expected to occur in an ingot mould and a continuously-casting ingot mould with an open nozzle will be the upper surface of the mould as schematically shown in Figure 5. The mould wall at the molten surface is considered to be always at the initial stage of the formation of a solid skin during pouring.

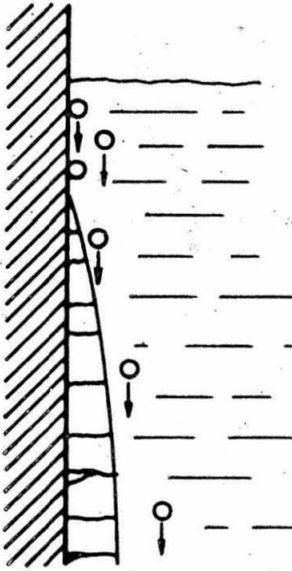


Fig.5 Origin of equiaxed crystals in a mould.

Figure 6 (a) shows a typical appearance of the top and the vertical section of the solid shell of a steel billet, produced in a continuous casting mould, which was obtained by elimination of the liquid by means of breaking out of the solid shell at about 1000 mm from the meniscus. The irregular shape of the top

of the resulting solid shell suggests that the top of the solid shell was at the unstable stage of the formation when the liquid was eliminated and that it was the place of the separation of equiaxed crystals.

When the pouring temperature is increased or when the rate of heat extraction is decreased, the place where the separation of crystals occurs will expand while it decreases when the pouring temperature is decreased or the rate of heat extraction is increased.

The place where the separation of equiaxed crystals occurs may move depending on the pouring temperature and the rate of heat extraction (24). Even when the molten metal touches on the mould wall, nuclei will be remelted if the temperature of the bulk liquid is high enough. Only when the nuclei can grow as neck-shaped crystals, the separation of the crystals will be expected from the mould wall to form the equiaxed zone.

It is obvious that when a cold substance is put on the molten surface or put into the molten metal, separation of crystals can be expected on its surface if the material is cold enough to form neck-shaped crystals, as schematically illustrated in Figure 7.

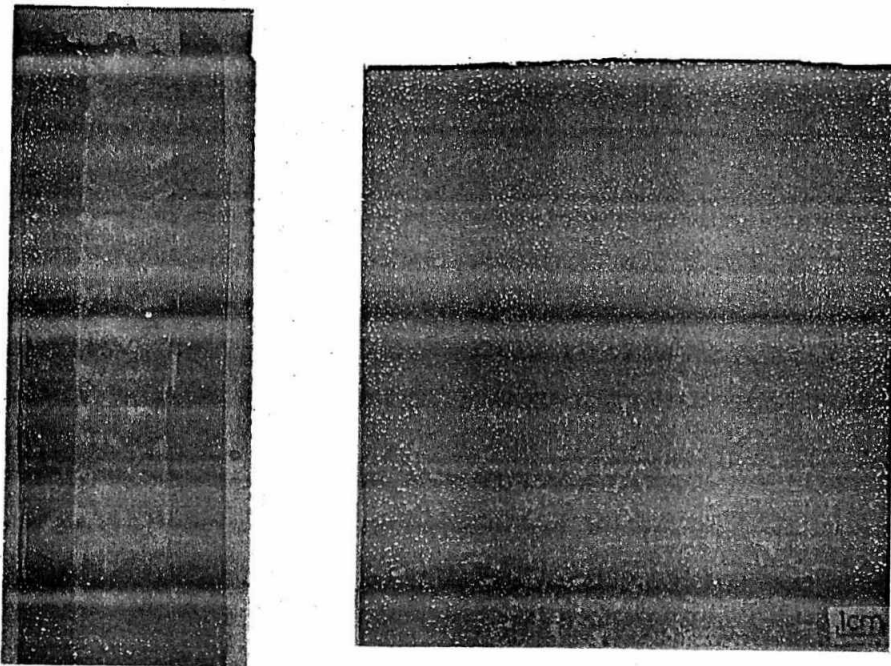


Fig.6 Typical appearance of (a) a vertical section of the solid shell and (b) the macrostructure of a steel billet.

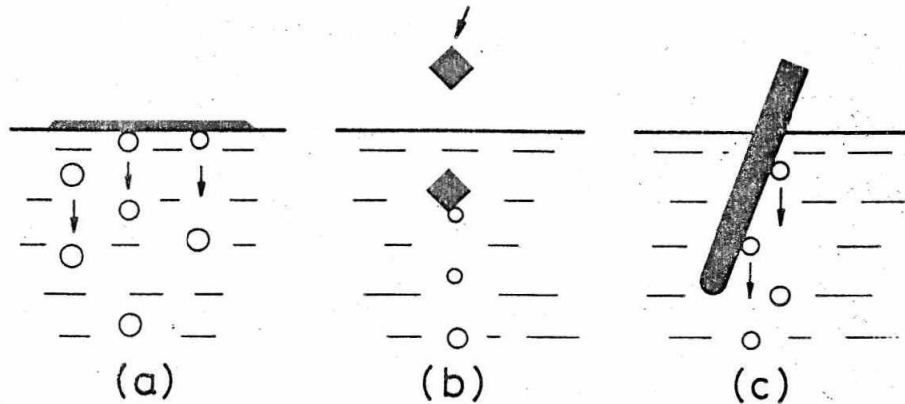


Fig. 7 Schematic illustration of the separation of crystals from (a) coverings, (b) additives, and (c) a cold bar.

FACTORS TO CONTROL THE FORMATION OF EQUIAXED CRYSTALS

Four major factors seem to control the formation of equiaxed crystals of steel ingots: 1) solutes or impurities, 2) mould, 3) motion of liquid in the mould, 4) pouring temperature.

Solutes:

When a molten metal is poured into a mould the metal is cooled by the mould with temperature far below its melting point. Therefore, the degree of undercooling in the molten metal is largest along the mould wall. Crystals which nucleate on the mould wall first tend to grow along it until the advancing front touches adjacent crystals to form a solid shell, as is schematically shown in Figure 2. The solid shell then grows forward forming columnar structure.

However, when a metal containing a soluble impurity which segregates at the advancing interface of solid and liquid during solidification, the segregation of the solute tends to prevent crystals from growing at their roots, forming narrow necked-shapes because the solute cannot diffuse into the mould wall, as is schematically shown in Figure 3.

Since undercooling of the liquid is most depressed at the root of a crystal on the mould wall, the depression prevents the crystal from growing along the mould wall. In other words, preferential growth of the crystal occurs at the side, forming a necked shape.

Tendency toward the formation of neck-shaped crystals on the mould wall, depends primarily upon the segregation

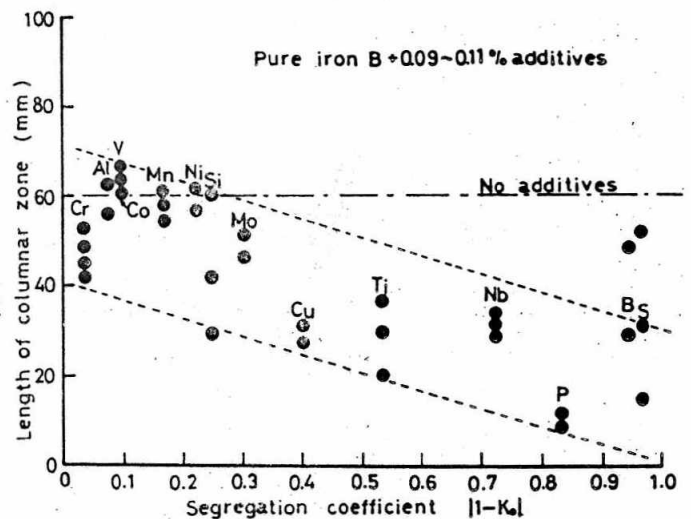


Fig. 8 The relationship between segregation coefficient of additives and columnar length of iron ingots.

coefficient of the solute. The solute with a large value of $|1-K_0|$ forms narrower neck-shaped crystals. This was clearly shown in the case of aluminium alloy castings (25).

Effect of small additives on the macrostructure of an iron ingot was studied (26). A tendency was observed that the length of the columnar zone of the resulting ingots, which was unidirectionally cooled from the bottom, decreased as the segregation coefficient of the additive element increased, though sulphur and boron showed variance of the result, as is shown in Figure 8. The variance is probably due to changing of the wetting property of the molten iron on the alumina mould wall by sulphur and boron. The addition of titanium, niobium, phosphorus and sulphur produced fine equi-

axed grains though sulphur showed variance. It is well known that titanium and niobium work as grain refiners for low carbon steels (20).

Until now common belief has been that some grain refiners act as nuclei of equiaxed crystals of cast metals. However, this can only be expected when particles of primary crystals of an alloy system are added into the molten metal at a low super heat. The primary crystals which remain as solid can grow, forming equiaxed crystals in the liquid (27).

Besides the segregation behaviour of solutes, the number of nucleation sites of iron crystals on the mould wall is considered to influence the grain size of steel ingots. Additives may change the properties of the molten surface, especially the properties of oxide films and nonmetallic substance, and then the wetting property of the molten metal onto the mould wall. This change in the properties must greatly influence the nucleation and the segregation of iron crystals on the mould wall during solidification. Therefore, the effect of the addition of each element must be discussed from the two points of view; first the segregation coefficient, and second, the number of nucleation sites on the mould wall. However, there is a lack of information of the nucleation and the separation of iron crystals on the mould wall so far.

Mould:

The second factor that affects the formation of equiaxed crystals of cast metals

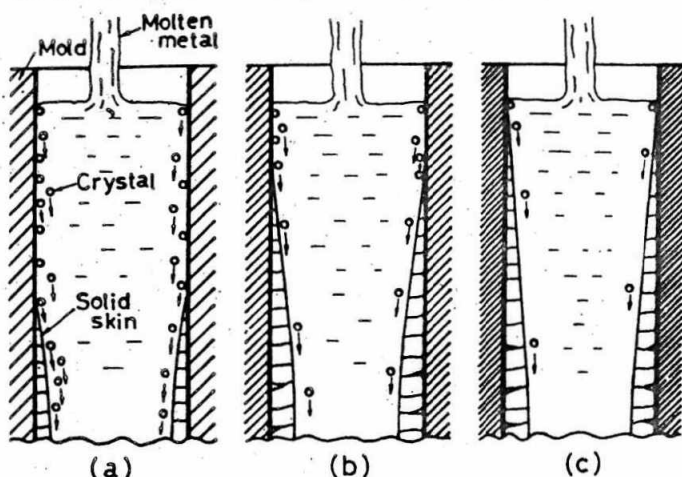


Fig. 9 Schematic illustration of the separation of crystals on the mould wall of three different heat extraction capacities.

is cooling condition of the liquid by the mould materials.

When a molten metal is poured into a mould with low cooling capacity, namely the ability of a mould to accept heat from a molten metal, the formation of a stable solid shell on the mould wall will be much slower than when it is poured into a mould with high cooling capacity. There is thus more opportunities in the former case for crystals to be separated away from the mould wall by molten flow or convection in the molten metal. An experiment with an ammonium chloride-water model clearly demonstrated this (10). Figure 9 schematically illustrates the effect of mould materials on the separation of crystals from the mould wall.

However, it must also be remembered that a mould with high cooling capacity is more suitable to prevent remelting of the free crystals, which were separated from the mould wall into the molten metal

Figure 10 shows the relationship between the average heat flux of the mould used and the area of the equiaxed zone in the case of aluminium ingots (28). This shows that increase of heat flux first increases the equiaxed zone and then decreases it because of the

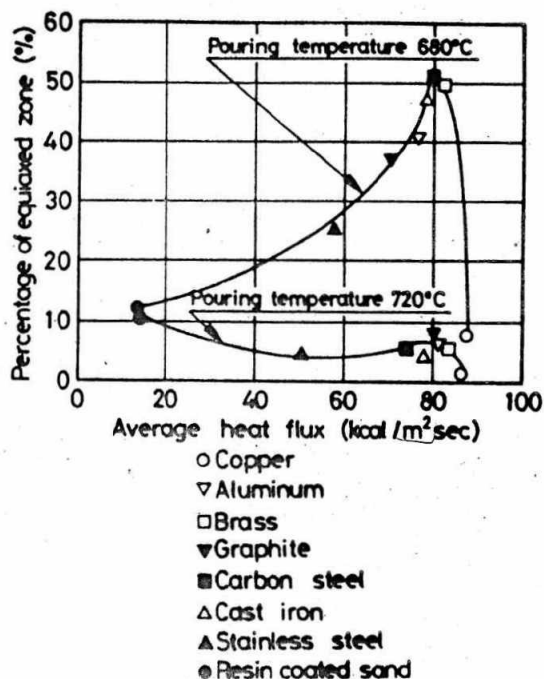


Fig. 10 The relation between average heat flux and equiaxed zone in aluminium ingots.

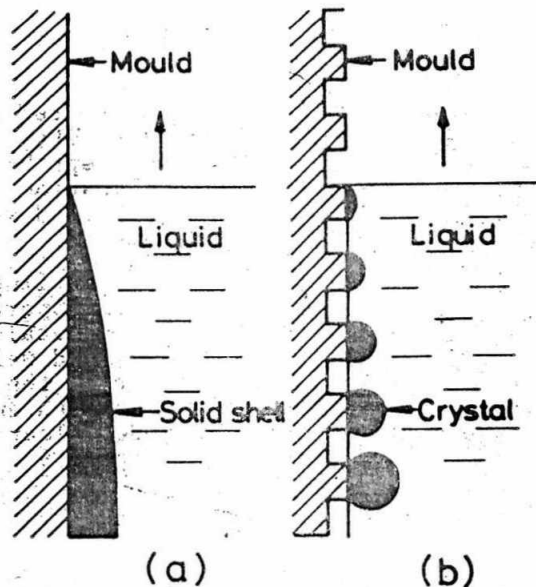


Fig.11 Schematic illustration of crystal growth on the mould wall.

promotion of the formation of a stable solid skin by rapid cooling. In other words, a high heat extraction mould prevents the separation of crystals from the mould wall.

Besides the cooling capacity, the roughness of the mould wall is very important. A rough surface promotes the formation of equiaxed crystals. In other words, a mirror surface mould promotes the formation of a stable solid skin forming the columnar zone in cast metals. In the case of the mirror mould there are no obstacles preventing the unbroken growth of crystals up the mould wall, as the liquid level rises, as schematically illustrated in Figure 11(a). With a rough surface if the cavities are large enough to prevent crystals is facilitated as schematically illustrated in Figure 11(b).

It is well known that the use of some mould coatings is often very effective for grain refining of cast metals (29). However, it is not well known why these compounds in the mould materials influence the grain size of the castings, in spite of the fact that they do not largely influence the grain size when they are added directly into the molten metal. Future studies must be concentrated on this field.

Motion of liquid:

Third factor that affects the formation of equiaxed crystals is the motion of

liquid. The separation of neck-shaped crystals is promoted by the motion of liquid. It most effectively promotes the separation of crystals from the mould wall at the initial stage of solidification of metals before the formation of a stable solid skin.

Various methods have been used to promote the formation of equiaxed crystals, such as, mechanical stirring (30-35), magnetic and electromagnetic stirring (35-39), sonic and ultrasonic vibrations (40-42) and agitation by gas bubblings (42). In all cases it has been believed that the principal mechanism for producing the equiaxed crystals is dendrite remelting (6). However, in the existence of dynamic motion in the liquid, neck-shaped crystals can be separated from the mould wall before the formation of the columnar structure. Therefore, the most effective way to produce equiaxed crystals is to promote the separation of crystals at the mould wall.

Multiplication of the free crystals, which were separated from the mould wall, will be promoted by forced vibration or agitation during the precipitation even after the formation of a stable solid shell, if they grow dendritically. However, surface vibration or agitation of molten metal along the mould wall is considered to be the best to promote the formation of equiaxed crystals since the top surface along the mould wall will always be at the initial stage of solidification, or at the unstable stage of a solid skin during pouring (43).

Pouring temperature:

The last but the most important factor is pouring temperature. To get a fine grain structure, remelting of separated crystals into the bulk liquid must be avoided as much as possible. Some free crystals having separated from the mould wall, will precipitate on the mould bottom, while some of the crystals float up in the liquid at the initial stage of solidification as schematically illustrated in Figure 12. Some floating crystals are remelted into the liquid, and some will be reduced in size by remelting. As the temperature of the metal decreases the floating crystals will precipitate to form the equiaxed zone.

Pouring temperature must be kept as low as possible to get a fine grain structure, because even when many crystals are separated from the mould wall at the

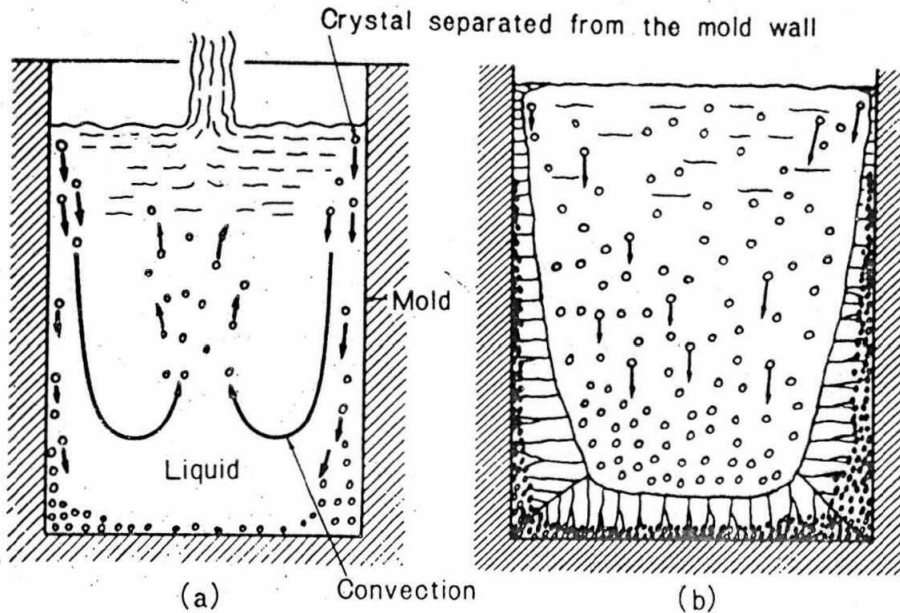


Fig. 12 Schematic illustration of forming ingot structure.

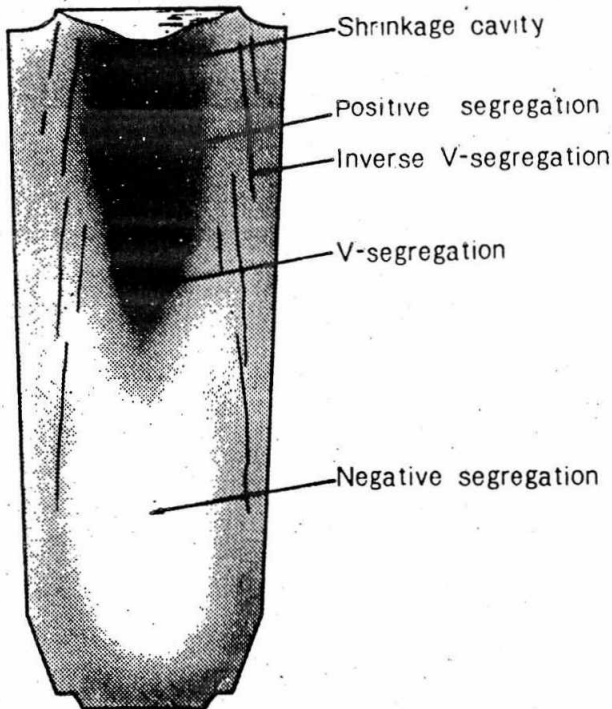


Fig. 13 Schematic diagram of macrosegregation in a steel ingot.

initial stage of solidification, they will be remelted into the liquid, forming a large coarse-grain structure.

MACROSEGREGATIONS

When a steel is cast in a mould, it is well known how hard it is to produce ingots which have uniform chemical com-

position. The type and location of macrosegregation are largely influenced by the physical properties of the components of the steels, the convection, the type of crystals growth, and the behaviour of the separated-free-crystals in the mould during solidification. Typical examples are V segregation, inverted V segregation, and negative segregation in large steel ingots. In most cases, microsegregation would be removed by annealing at a high temperature; however, the macrosegregation cannot be removed by annealing and is carried over to the final products.

Inverse segregation, known as negative segregation, is often observed in the lower central portion of large steel ingots. The formation of negative segregation in steel ingots has previously been explained by the precipitation theory (44). But it has not been possible for this theory to explain why carbon content in the center of a crystal in the negative segregation zone is much lower than that of the outer columnar crystals.

Even if the precipitated crystals nucleate in the solute-concentrated liquid in front of the advancing columnar crystal zone, or even if the crystals separate from the dendrite arms of the advancing columnar zone by dendrite remelting, it is impossible to explain why the carbon content in the crystals of the negative segregation zone is lower than that of the outer columnar crystals. The crystals with the lowest carbon content in

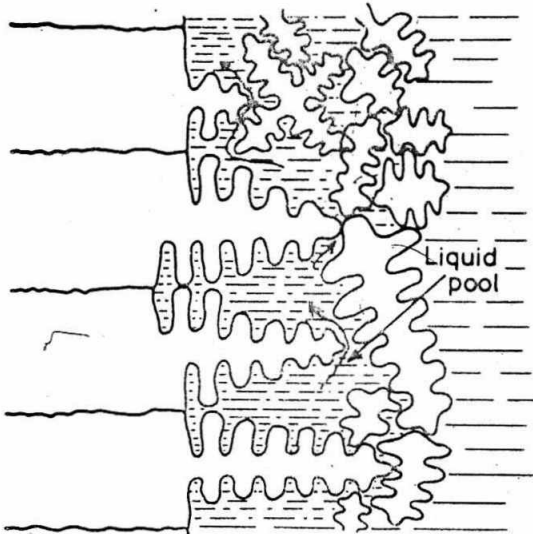


Fig.14 Schematic illustration of formation of string-type inverted V segregation.

a steel ingot can only form in the initial stage of the solidification.

The formation of negative segregation in large steel ingots is thus due to the separation and precipitation of relatively pure iron crystals from the mould wall in the initial stage of solidification.

Segregation of sulphur, phosphorous, and carbon can form in V and inverted V form in killed steel ingots as schematically shown in Figure 13. V segregation is probably produced by the dropping of the central precipitated crystal zone which had been formed by free crystals separated from the mould wall.

The formation of inverted V segregation has been considered to be due

to the upward movement of the solute enriched liquid along the solidification front in an ingot (45,46,47).

The observation of the solidification phenomenon in an ammonium chloride-water model suggests that when free crystals precipitate onto the tips of the growing front of the columnar dendrites of the solid shell, liquid pools form between the dendrites, and when the density of the interdendritic enriched liquid in the pools decreases, the liquid in the pools start to flow upward connecting with other pools to form liquid channels as schematically shown in Figure 14. The liquid in the channels finally forms string-type inverted V segregation.

It was reported that the lowering of the silicon content or the addition of molybdenum into the molten steel greatly changed the dendrite morphology and eliminated the inverted V segregation (48,49).

HOT TEARING

The external hot tears which start at the outer surface of an ingot and proceed inward are often seen in steel ingots. This type of hot tear is mostly caused by the formation of an irregular thickness of solid skin during the initial stage of solidification. The solid skin thickens irregularly when the molten metal rises up in the mould discontinuously, when the thermal conductivity of the mould surface is not uniform, or when the molten surface is prevented by gases, oxides, or scum on the surface of the molten metal from coming in contact with the mould wall.

As shown in Figure 15a, when the thicker section of the solid starts to

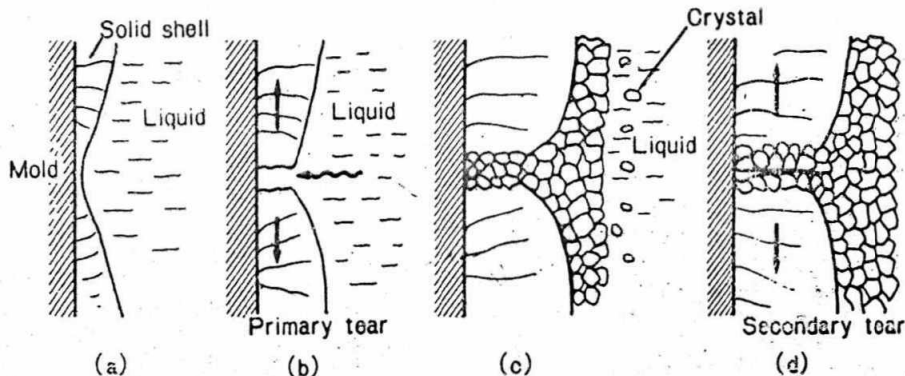


Fig.15 Schematic illustration of the process of forming a hot tear in an ingot during the solidification.

shrink, the thinner part of the solid skin will be broken and will form the primary tears. Hot tears can be filled in with enriched solutes. Therefore, during the cooling of the ingots, secondary tearing may also occur at the place where primary tearing had originally occurred.

CONCLUSION

First, the formation of equiaxed crystals in the steel ingots was discussed. Then, based on the new separation theory, the control of the structure of the steel ingots, the formation of macrosegregation, and hot tearing were explained. Also, suggestions were made on how to prevent the occurrence of certain problems related to the above process. These suggestions also come from the new separation theory.

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