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Author(s)	Takahashi, Tadayoshi; Kudo, Masayuki; Hagiwara, Iwao
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The Formation of Crystals and the Sedimentation Phenomena by Stirring of the Upper Part of Molten Metal

Tadayoshi TAKAHASHI*

Masayuki KUDO*

Iwao HAGIWARA*

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Abstract

In order to investigate the relation between the growth morphology of crystal and the conditions under which the crystals were formed during solidification, the upper part of a molten metal was stirred along the mould wall from just above liquidous temperature to an appropriate temperature.

As a result, very fine and sphere-like crystals were observed after solidification. It is considered that the dendrites crystallized during solidification could be readily shattered by the resistance of flow of the residual molten metal.

Further, the upper part of the molten metal was continuously stirred during solidification of the Al-Cu alloy and carbon steel.

The results obtained were as follows ;

Fine crystals were continuously accumulated upward from the bottom of the ingot, and the upper part was maintained in a molten state up till the time of final solidification. The resulting ingots with the fine crystals have a flat top surface and a homogeneous distribution of solute concentration.

1. Introduction

Two origins have been considered for the formation of the equiaxed crystals¹⁾²⁾. The first hypothesis has it that nucleation of the equiaxed crystals occurs when the liquid reaches its heterogeneous nucleation temperature, as a result of constitutional supercooling. The second proposal is that the nuclei originating in the chill zone are carried by convection to the center of the melt, where they grow to produce the equiaxed crystals. In addition to the two theories described above, it has also been suggested that many detached crystals are produced by partial remelting of dendrites, which give rise to the equiaxed crystals.

* Department of Metallurgical Engineering, Faculty of Engineering, Hokkaido University, Sapporo, Japan.

However, little is known as to how the fine detached crystals grow during solidification or how they change by the surrounding conditions.

Thus, in order to examine the growth process of the crystals, the authors produced fine detached crystals at the upper part of a melt, using a special technique named "stirring solidification of the upper part", and the macro- and micro-structure were observed.

Using this technique it was noted that solidification advanced upwards from the bottom of the mould.

As a result, it was found that the ingot in its entirety as produced at a laboratory-scale consisted of the fine crystals. It was proposed that this technique may be applied as a new method in ingot solidification.

2. Experimental procedures

The materials used in the present investigation were an Al-4wt pct Cu alloy and carbon steel (S45C). The mould of the Al-Cu alloy was a graphite crucible with an internal diameter of 3 cm, height 12 cm and thickness 0.8 cm, and the height of the melt was 7 cm.

The liquid alloy was stirred at 700°C to ensure complete homogenization, and after which the electric power input was turned off. The upper part of the melt was stirred along the mould wall with a rotation speed of 60 cpm from 652°C to an appropriate temperature or final solidification using a preheated steel rod of 0.2 cm in dia. which was inserted into the melt to a depth of

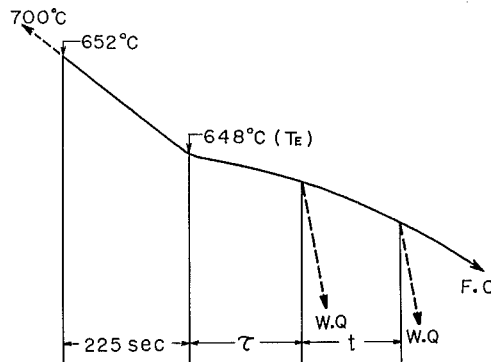


Fig. 1. Cooling process for observation of the formation of crystals and sedimentation phenomenon in an Al-4wt pct Cu alloy.

t : Furnace cooling time

τ : Stirring time from T_E

T_E : Equilibrium solidification temperature in an Al-4wt pct Cu alloy

about 3 cm. The direction of rotation was alternately reversed.

The relation between the cooling process of the melt and the stirring time is shown in Fig. 1. In the case of furnace cooling, the time of stirring from 652°C to equilibrium solidification temperature T_E , (648°C) was 225 sec on the average and it was the same in all of the present experiments in an Al-4wt pct Cu alloy.

The stirring time from T_E is shown as τ in Fig. 1. The time was selected according to the purpose of each experiment. Therefore the sum of τ and 225 sec expresses the total stirring time.

After completion of stirring, the ingot was cooled in either of the following three ways; quenching in water immediately without furnace cooling or quenching in water after furnace cooling for t sec or complete furnace cooling.

The operations above-mentioned were carried out by measuring the temperature changes with thermocouples inserted into the center of melt to a depth of about 4.5 cm. Thermocouples of chromel-alumel wire were used without protecting the bead to ensure rapid response to temperature changes.

The cooling curves were recorded with an electronic recorder and a micro-voltmeter to amplify the temperature change.

For carbon steel, an alumina crucible was used as a mould, and the size of ingot was 5.5 cm in dia. and 15 cm in height. The weight of an ingot was 2.5 kg. The material melted in a tammann furnace was cooled according to the following procedure; the melt was slowly cooled to 1550°C after de-oxidizing at 1580°C, and then stirred with a quartz tube of 0.6 cm in dia. in the same manner as that in the Al-Cu alloy. The stirring was continued until the accumulating crystal layer reached the top of the ingot.

The specimens in an Al-4wt pct Cu alloy and carbon steel were cut along the length through the center line of the ingots, and were mainly etched with a 2 pct sodium hydroxide solution and Oberhoffer's reagent.

In the above experiment, first, the sedimentation phenomenon of dispersed and detached crystals after the cessation of stirring was observed, and secondly, the morphology of crystals in the solidified ingot were also observed in the case of continued stirring to final solidification.

3. Experimental results

3.1 Crystal formation and sedimentation phenomenon

Photo. 1 (a) shows the macrostructure of an Al-4wt pct Cu alloy. In this case, the total stirring time was 270 sec, and the stirring time τ from the equilibrium solidification temperature T_E to 647°C was 45 sec. Then the ingot was water-quenched after cessation of stirring. The cooling curve of the alloy

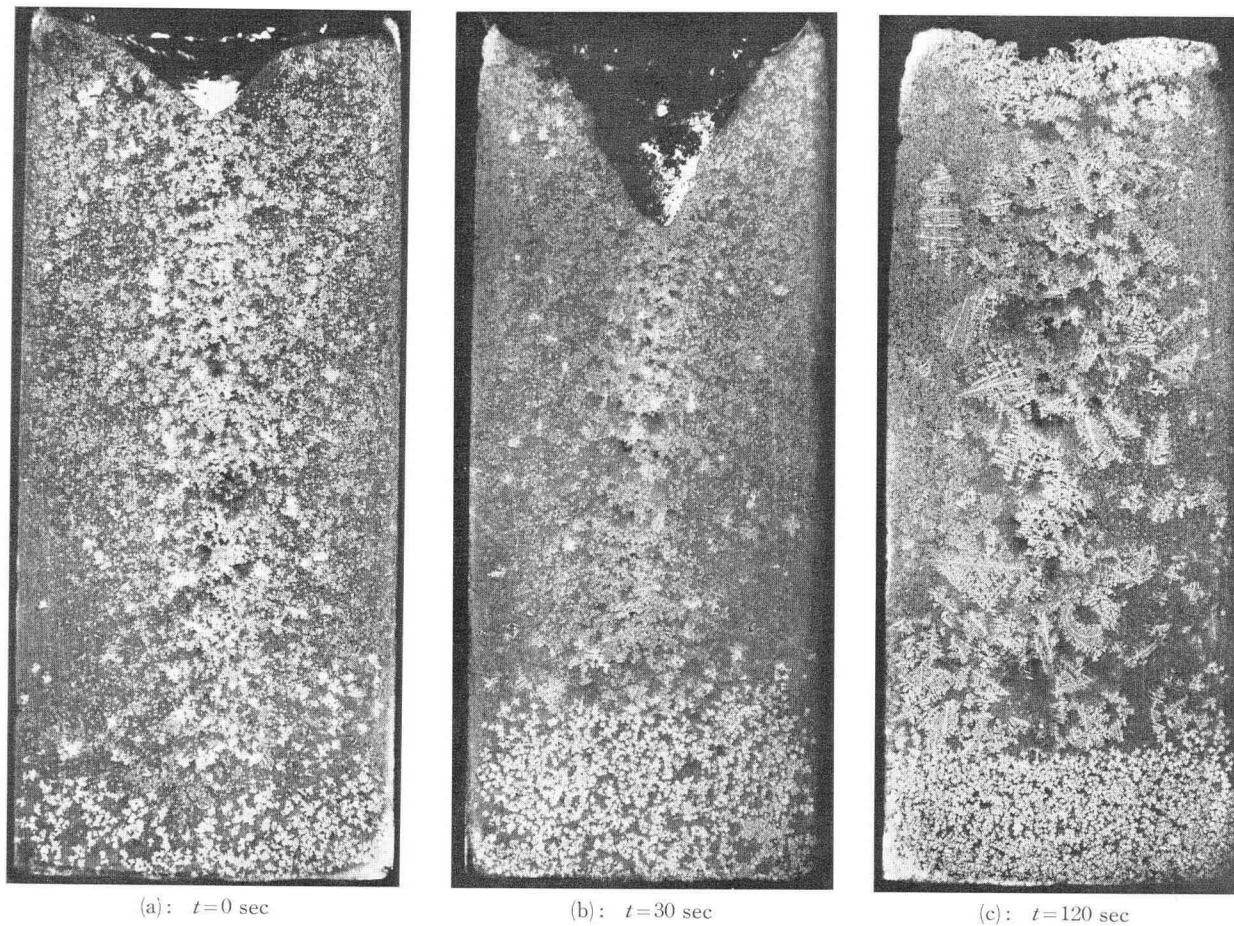


Photo. 1. Crystal formation and sedimentation phenomenon in an Al-Cu alloy.
Etched by 2% NaOH solution $\times 1.5$

is shown in Fig. 1.

It was observed that fine and snow-like crystals were distributed at random in the cross section of the ingot. A more detailed examination showed that a nebula like grouping was present and that some of them accumulated at the bottom of the ingot. The process of crystal growth was clearly observed.

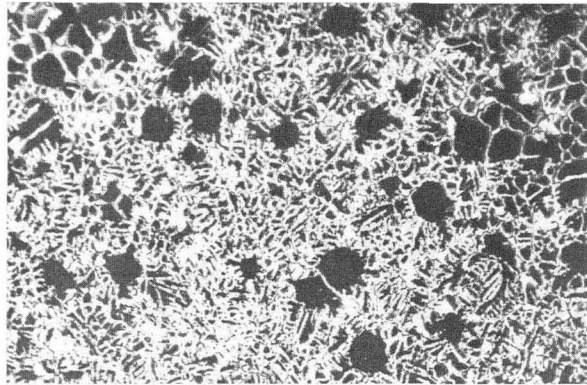
In photo. 1 (b), the total stirring time and the stirring time τ from T_E in Fig. 1 were similar to those in photo. 1 (a), and the specimen was quenched in water after furnace cooling for 30 sec. It was observed that the number of crystals formed and the amount of sedimented crystals were in excess of those of photo. 1 (a).

The stirring times in photo. 1 (c) were the same as those in photos 1 (a) and (b), and the specimen was water-quenched after furnace cooling for 120 sec. It was observed that the amount of fine crystals was approximately similar to that of photo. 1 (b), and large and free dendrites were also observed in the central part of the ingot, and were not observed in a settled state at the bottom part. It was also interesting that a curved dendrite was seen at a one-third height from the bottom along the center of the ingot.

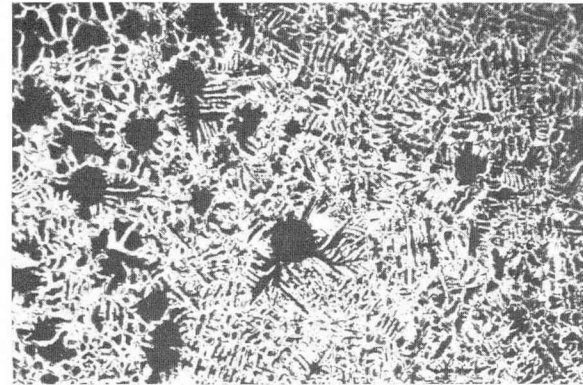
It was deduced from the above observations that the sedimentation rate of small and spherical crystals which exist at the bottom of ingot may be more rapid. It was observed that these crystals existed in a packed state, close to each other. This may be explained as follows. The state of sedimented crystals was maintained without crystal growth owing to reciprocal interference. On the other hand, the crystals at the upper and middle parts of the ingot grew to large and needle-like dendrites which were suspended in the melt without sedimentation. Such differences are considered to be caused by the initial surrounding conditions of the crystal formation.

Next, crystal morphology was investigated by means of microscopic observation. Photo. 2 (a) shows a portion near the course of movement of a stirring rod in photo. 1 (a). Photos. 2 (b) and (c) show the center part and a part one quarter distance from the side of the ingot, respectively, at a depth of about 3 cm below the top of the ingot of photo. 1 (b). Photo. 2 (d) is the photograph of sedimented crystals at the bottom part of the ingot in photo. 1 (c). The size of black particles in photo 2 (a) are 50 to 100 μ in dia. and their shape is almost spherical. It may be noted that some of particles are small, probably because of dissociation. On the other hand, the particles in photo. 2 (b) show branches growing to some favorable orientations. Moreover, the crystals in photo. 2 (c) are originally needle-like which are expected to develop maintaining their original forms.

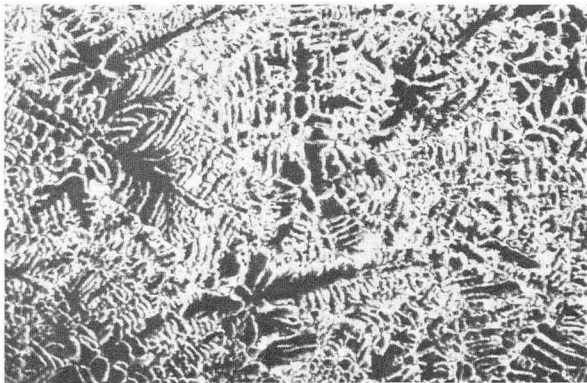
In the present experiment, the dispersion of forming crystals by a stirring



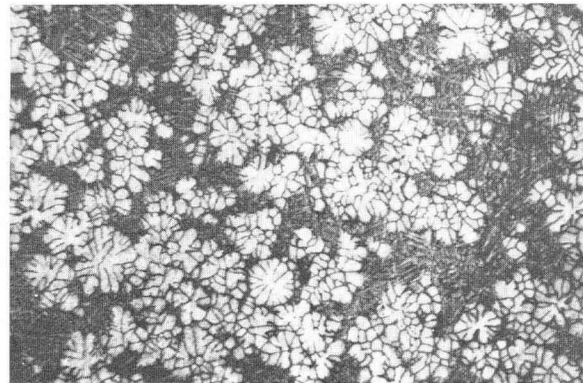
(a) Spherical crystals
× 40



(b) Dendrite branches originating from
spherical crystal × 40



(c) Needle-like dendrites
× 40



(d) Chrysanthemum petal like
crystals × 13

Photo. 2. Various shapes of crystal growth.

rod was easily performed under slow cooling conditions rather than rapid cooling, and at the same time, stirring was readily carried out even after crystals were almost formed.

Furthermore, since the temperature and concentration of the residual liquid are easily made uniform within the range of stirring effect, it is considered that the dispersed and detached crystals in this range grow under a condition of no gradient of temperature and concentration. Therefore, the crystals readily become spherical. The condition is similar to the initial stage of formation of equiaxed crystals in the usual solidified ingot. Some of the detached and dispersed crystals might be somewhat irregular, but they are also considered to be made more spherical by the shearing force of the viscous fluid during solidification, in addition to the effect of temperature distribution and solute distribution described above.

For photo. 2 (d), it is characteristic that many crystals grow uniformly to a shape resembling chrysanthemum petals.

On the other hand, fine and nebula-like crystals which exist near the center part of the ingot are hardly effected by stirring. Therefore uniformity of temperature and solute concentration and the effect of the shearing force of viscous fluid can not be considered in this portion. As a result, the crystals may well develop into the same dendrites as those formed in the usual solidification.

It has been clarified that the branches of needle-like dendrite in the easiest growing directions are determined by the effect of the temperature and solute distributions.

The above phenomena is known not only for metal but also for ice³⁾ and snow crystals⁴⁾.

3.2 Sedimentation rate of the spherical crystal

It was recognized that the spherical crystals easily fell to the bottom of the mould by sedimentation. The sedimentation phenomenon of spherical crystals were examined using Stoke's law, which describes the motion of a free solid ball falling in a viscous fluid under gravitation.

In the case of applying Stoke's law, the size of the solid ball is subjected to a restriction. The maximum radius should be approximately $2 \times 10^3 \mu$.

The radius of crystals observed at the upper part of ingot is 25μ and the sedimented crystal is on an average 250μ . The radius of the crystal is assumed not to change during the falling process. Therefore Stoke's law can be applied to the present experiment.

The sedimentation rate may be calculated for the radii of 25 to 250μ from the following formula;

$$v = \frac{2gr(\rho_s - \rho_L)}{9\eta}$$

- v : sedimentation rate, cm/sec.
 g : gravitational acceleration,
 η : viscosity of molten metal, (5.5×10^{-3} gr/cm·sec)⁵⁾
 r : radius of crystal, (25~250 μ)
 ρ_s : specific gravity of solid phase in an Al-4wt% Cu alloy
 (2.55 at 648°C)⁶⁾
 ρ_L : specific gravity of liquid phase in an Al-4wt% Cu alloy
 (2.47 at 648°C)⁶⁾

From the results of calculation, the sedimentation rate for a crystal of 25 μ in radius at the upper part of the ingot is 1.88×10^{-2} cm per sec and the rate for the crystal of 250 μ in radius at the bottom part of the ingot is 1.88 cm per sec. The latter value is one hundred times larger than the former.

Moreover, the sedimentation phenomenon was examined for the initial stage of formation of the crystals in photo. 1(a) corresponding to the above results, assuming that the crystals fell from half of the stirring depth of about 3 cm below the top of ingot. If the crystal formed at the upper part falls at once, without any stagnation, the falling time is 45 sec. The sedimentation rate of crystals which are at first accumulated is 0.122 cm per sec.

On the other hand, the radius of sedimented crystal can be predicted from the sedimentation rate. The sedimentation rate of 0.122 cm per sec corresponds to a radius of 75 μ , which is somewhat smaller than the mean value between 25 μ and 250 μ , respectively, observed at the upper part and bottom part of the ingot.

However, stagnation of falling of crystals is considered to occur actually by stirring in the upper region, and the crystals may probably grow during sedimentation. Therefore the initial sedimentation rate at the upper part will be approximately 1.8×10^{-2} cm per sec corresponding to the crystal of 25 μ in radius, and the sedimentation rate at the lower part will approach the rate of about 1.88 cm per sec corresponding to the crystal of 250 μ in radius since the crystal might grow during sedimentation.

3.3 Application of the stirring solidification of the upper part

The authors have previously proposed a method of scrape-solidification as a technique for ingot solidification in order to obtain fine grains and to protect solute segregation⁷⁾.

The outline of this technique is as follows; the surface of transitional solidification zone is scraped to a optional depth with a rod, in such a way

that the dendrite tips become separated. Moreover, as a secondary effect accompanied by stirring of the viscous fluid, a large number of eddy currents might occur behind the stirring rod and they might be transmitted to the surroundings in the same manner as heat transfer, reducing the current. Thus the fine detached crystals might be dispersed uniformly in the liquid. The number of crystals can be increased by continuing the scraping. If the melt is scraped until it becomes a pasty state, the inner region close to the scraped position may be solidified with a uniform distribution of fine crystals, and at the same time a mutual mixing action of crystals may also occur. As a result, ingots with reduced segregation and non-metallic inclusions were obtained.

In short, it was found that the phenomenon produced by the action of scraping was due to a crystal multiplication rather than nucleation.

In the stirring solidification of the upper part as against the scrape-solidification, the upper part of the ingot was continuously stirred from the molten state to the end of solidification. As a result, the phenomena of detachment and sedimentation of forming crystals took place. Thus, the primary crystals were dispersed, their shape became sphere-like and their size remained fine.

Furthermore, continued stirring results in successive accumulation of the fine crystals to the upper region, and an ingot comprised entirely of fine crystals was obtained.

The materials and the mould used in the present experiment were the same as those described in the previous section. The experiment with an Al-4wt pct Cu alloy was performed according to the cooling process as shown Fig. 1. The stirring time from equilibrium solidification temperature T_E is τ in the cooling process.

Photos. 3(a), (b) and (c) show the change of the accumulation of fine crystals from the bottom of the ingot with increasing τ , namely, τ is 75 sec in (a), 130 sec in (b) and 180 sec in (c), respectively. Thus the total stirring time is equal to τ plus 225 sec. Each specimen was subjected to continuous cooling in a furnace after stirring was ceased. Coarse dendrites were formed in the residual liquid above the region of fine crystals.

Photo. 4 shows the macrostructure of a case in which stirring solidification of the upper part is applied to carbon steel until the accumulating crystal layer reaches the top of the ingot. The upper part of the ingot was close to a liquid state till the completion of the solidification and hence the stirring of the upper part was easily performed. The coarse dendrites, which are seen at the bottom part of ingot in photo. 4, may be due to the effect of the form of the crucible

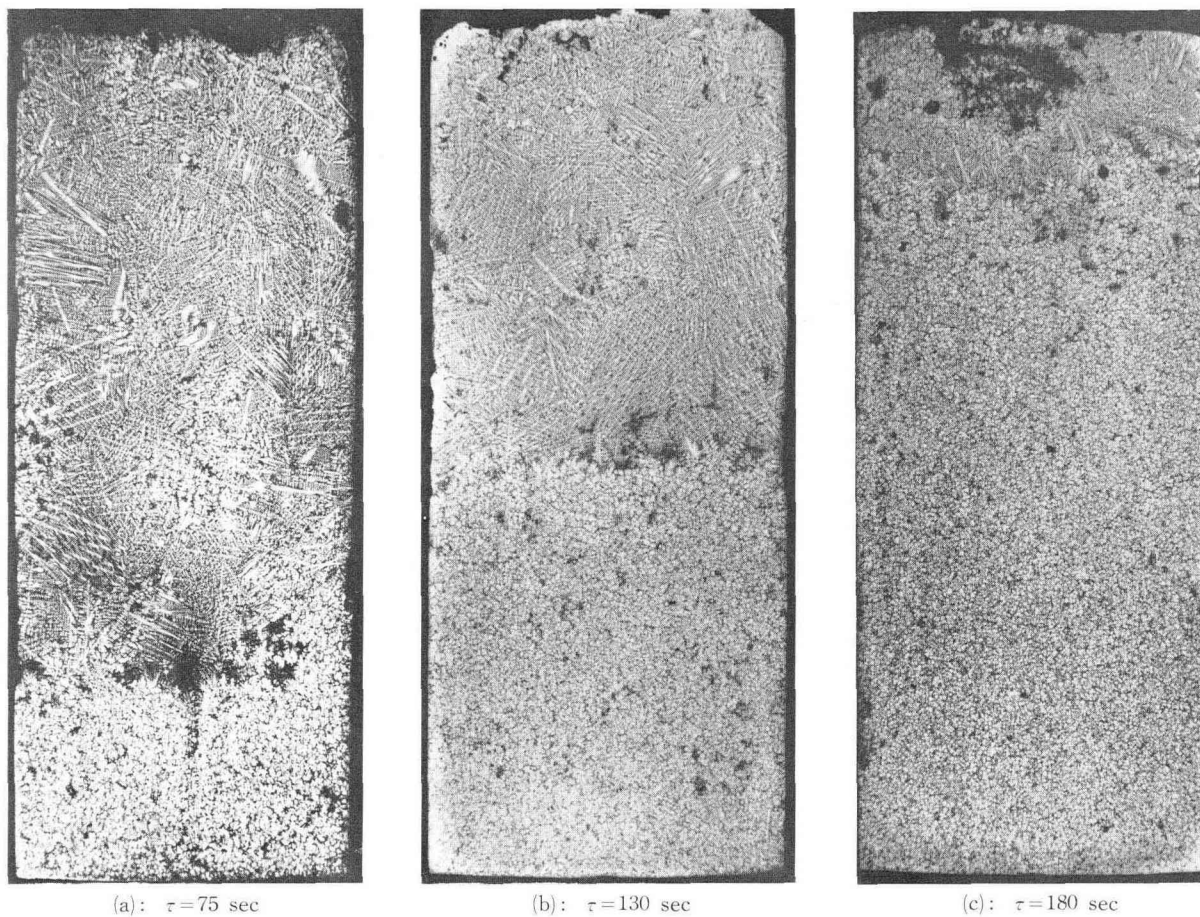


Photo. 3. Accumulating process of fine crystals by stirring solidification of upper part with increasing of τ . Etched by 2% NaOH solution. $\times 1.5$

used. The region above the bottom part consisted of fine crystals. In proportion to the stirring time of the upper part, fine crystals occurring tended to be accumulated layer upon layer from the bottom to the top of the ingot. Therefore, it is characteristic of the present technique that the solidified ingot has a flat top surface and shows no shrinkage pipes.

Furthermore, as understood from the crystal formation and sedimentation phenomenon in the Al-4wt pct Cu alloy described above, the formation and dispersion of the crystals occurred simultaneously at the upper stirring region. The dispersed crystals settled from the upper part, and new crystals formed again in this region. Accordingly, the upper part of the ingot was the source of the supply of fine crystals. As a result, the phenomena of crystal formation, the dispersion-spheroidization and sedimentation were repeated successively till final solidification.

Moreover, since the accumulation of spherical crystals was continuously performed from the bottom to the top of the ingot, the supply of the residual melt accompanied with solidification shrinkage was done more smoothly than that in usual solidification. Therefore, the ingot obtained had no pinholes or shrinkage pipes.

The comparison of macro-segregation between the usual solidification and stirring solidification in the same conditions is shown in Figs. 2 (a) and (b) for an Al-4wt pct Cu alloy. In the figure,

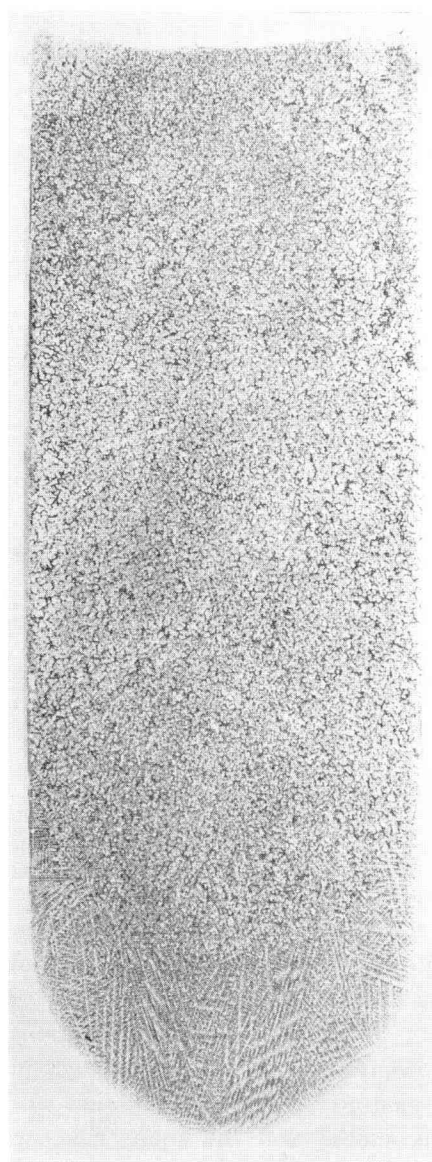


Photo. 4. Macrostructure with fine crystals by stirring solidification of upper part in carbon steel. Etched by Oberhofer's reagent.

× 1.0

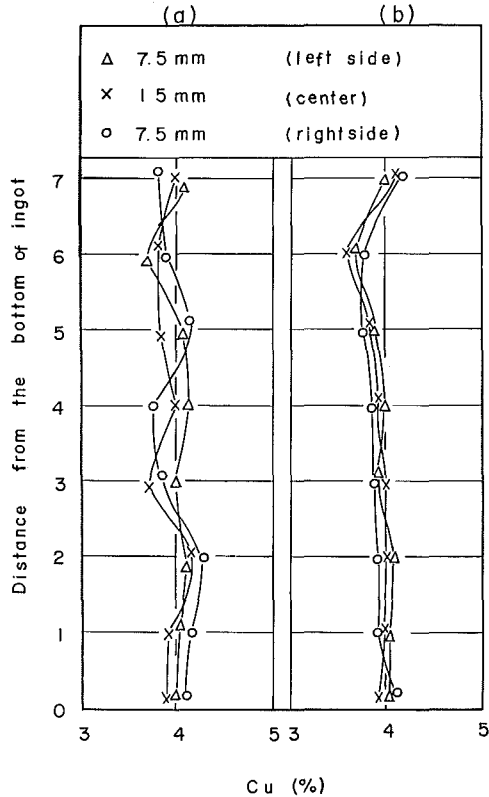


Fig. 2. Comparison of macrosegregation between the usual solidification (a) and stirring solidification of the upper part (b) in an Al-4wt pct Cu alloy.

each value is the solute concentration at the symmetric position of 0.75 cm distance from the side surface and at the center line of longitudinal cross section of the ingot.

In the case of the conventional solidification in (a), gravity segregation is recognized. On the other hand, in the ingot of photo. 3 (c), which was subjected to stirring solidification of the upper part, macrosegregation was not recognized and the solute concentration is approximately 4pct in the region where the fine crystals accumulate as shown in Fig. 2 (b).

There is a restriction of the solidification rate in the application of the stirring method of the upper part. The relation between the solidification rate and the stirring time of the upper part is shown in Fig. 3.

The experiment was performed under conditions of the same mould size for an Al-4wt pct Cu alloy described above. As a result it was found that

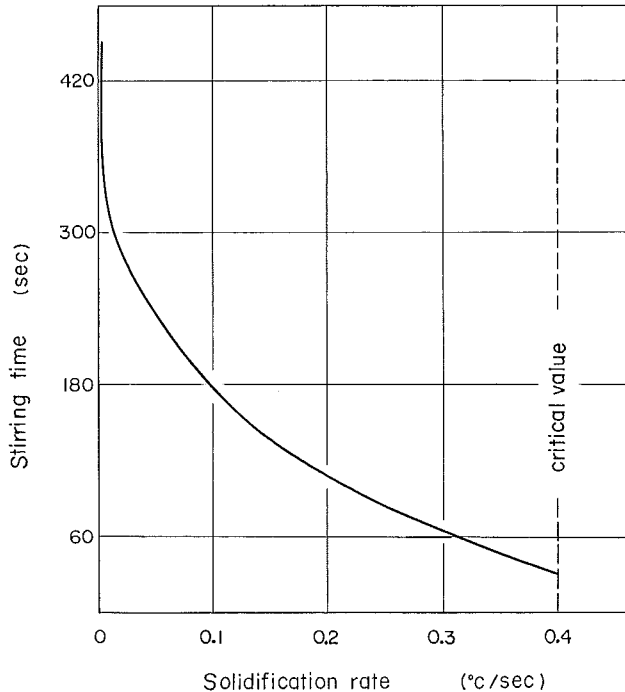


Fig. 3. Relation between solidification rate and stirring time.

the stirring solidification of the upper part could be performed to a critical value of the solidification rate of 0.4°C per sec when the stirring time was 30 sec. If the solidification rate exceeded the above value, the phenomenon seen in the scrape-solidification occurred in spite of the stirring solidification of upper part.

4. Conclusion

- (1) The separation and dispersion of dendrites, which were initially crystallized from the melt, occurred by the shearing force of the flow of molten metal produced by stirring, resulting in a very fine and spherical crystals.
- (2) The crystals were readily changed to various shapes by the temperature and solute distributions environment and in some cases the dendrites were partially remelted off and became fine detached crystals or they grew to needle-like forms rather than sphere-like crystals.
- (3) The present experiment showed that the spherical crystals showed a strong tendency to fall to the bottom of the mould in spite of a slight difference of specific gravity between the crystals formed and the melt, while the

needle-like crystals remained in the region where they grew.

(4) Based on the above results, when the stirring at the upper part of the melt was carried out from the molten state to the terminal solidification, the upper part of the melt was the source of supply of fine crystals, and the crystal formation, the dispersion-spherodization and the sedimentation phenomenon were repeated successively during solidification. As fine crystals were continuously accumulated upwards from the bottom of the mould, the ingots obtained, showed a flat top surface and a homogeneous distribution of solute concentration.

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