Undercooling in Al–4 wt. % Cu Alloy

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Abstract

Undercooling is one of the most fundamental solidification phenomena. A study on this phenomenon was made on bulk specimens of an Al–4 wt. % Cu alloy cooled by spraying water onto the graphite crucible. In the experimental results, when undercooled to more than 15°C, the solute concentration of the primary crystal was increased to a saturated value of approximately 2 wt. % Cu which showed a deviation from the saturated value of the equilibrium solidus line owing to precipitation of θ phases. When the primary crystal was undercooled below the equilibrium of eutectic temperature, the microstructure was not dendritic. The structure showed clear subgrain boundaries and spherical θ phases which were homogeneously distributed not only on the grain boundaries but also in the grains.

1. Introduction

Undercooling phenomenon is invariably observed to a certain extent in practical casting processes. It can be said that this phenomenon is one of the most fundamental solidification phenomena. On one hand, the structure and segregation must be controlled to improve the mechanical properties of the metal material. And the undercooling phenomenon may be considered as one of the methods for the control of the above. In the present paper the changes of solidified structures under various degrees of undercooling are investigated together with the relation between the solute concentration of the actual primary crystal and that of the solidus line in the equilibrium phase diagram, using an Al–Cu alloy. In addition various factors influencing undercooling are described.

2. Experimental Procedure

Undercooling is generally obtained by increasing the cooling rate[1]. The

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formation of crystals caused by quenching methods is in general influenced by the temperature gradient, cooling rate, the action of heterogeneous nuclei etc.. Thus, it must be recognized that solidification begins in the vicinity of the ingot surface which is firstly cooled. It has been reported that the growth rate of crystals which are formed from the melt is approximately proportional to the square of degree of undercooling. The relation is $V=A(\Delta T)^B$, where V: crystallization rate (cm/sec), ΔT: degree of undercooling (°C), A: const. and B: 1.7–2.0[2]. The metal which has a large quantity of latent heat and small specific heat will show strong recalescence. The maximum recalescence temperature is raised at times to the equilibrium liquidus temperature. Thus a cooling method must be designed to prevent the temperature from rising with recalescence because the condition of solidification differs between the primary crystal and the subsequent crystal which forms. As there is a limit to the increase of cooling rate, ingot weight and quenching method must be utilized in order to produce sufficient undercooling in the centre of the specimen. Various quenching methods for an Al–4 wt. Cu alloy were examined, and the equipment shown in Fig. 1 was used. The ingot weight was about 10 g. A Chromel/Alumel thermocouple wire 0.3 mm in dia. was set without protection in the centre of half height of charge so as to assure a rapid response.

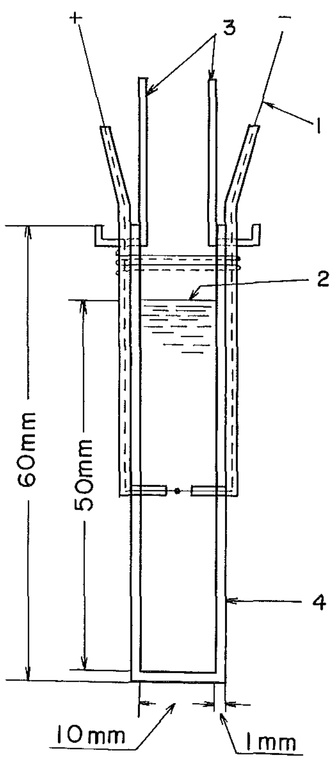


Fig. 1. Cooling method by spraying water
(1) C–A thermocouple
(2) Molten alloy
(3) Holder
(4) Graphite crucible

In the experimental procedure, first an Al–4 wt. % Cu alloy weighing about 1 kg was melted and held at 800°C. The molten alloy flowed into a preheated graphite crucible with a thermocouple the crucible (with which became a mold later) immediately after the crucible was immersed in large quantity of melt. Then the crucible containing the melt was cooled by spraying water of a given temperature. In the quenching methods to cool two sides of the small crucible by spraying water was found to produce the best results.

It depends upon the accuracy of the recorder to assure a rapid response.

Thus an electronic autoequilibrium recorder with an equilibrium speed of about 1 sec for the full scale of 150 mm was used together with a highly sensitive microvoltmeter, so that the temperature range could be predicted and expanded. The chart speed was 150 mm/min.

A small ingot cooled rapidly by spraying was transversely severed at a distance of about 1 mm from the thermocouple. After the sample was polished and etched, it was stamped with a microhardness tester at the required positions of the microstructure. Metallographic samples were again polished and then removed for electron probe microanalysis. It was determined that the solute concentration of the primary crystal was the average concentration of all primary crystals except for precipitates, interdendritic arm spacings and their neighbourhoods. The concentration was quantitatively obtained by relative intensities of the sample to Cu and $CuAl_2$. The molten alloy was mixed thoroughly and a small quantity was sampled by a quartz pipe in order to run a chemical analysis. The average solute content of bulk samples was between 4 ± 0.1 wt. % Cu. The degree of undercooling was measured as the difference from the equilibrium liquidus temperature (648°C) for Al–4 wt. % Cu alloy.

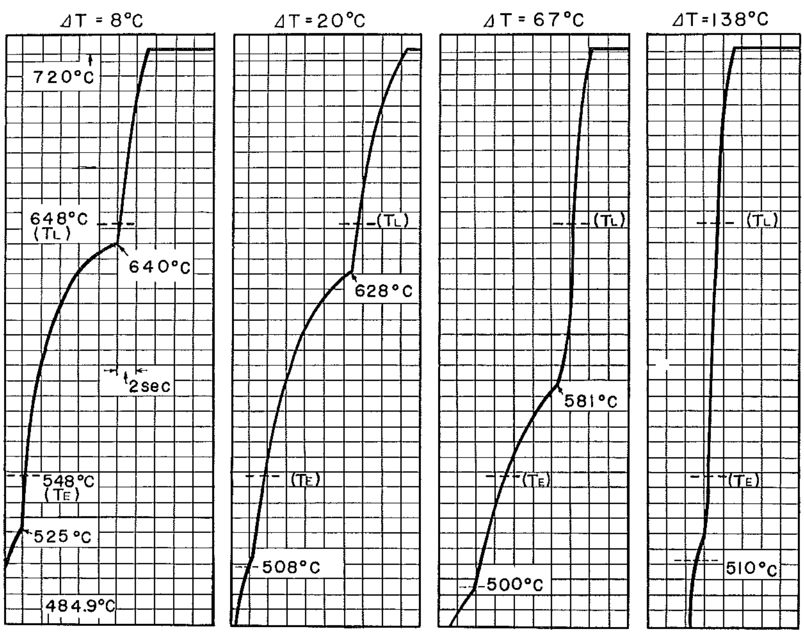


Fig. 2. Cooling curves obtained by chilling of Al–4 wt. % Cu alloy.
T_L : Liquidus temperature of equilibrium solidification
T_E : Eutectic temperature of equilibrium solidification
ΔT : Degree of liquidus undercooling

3. Experimental Results

3.1 Degree of Undercooling and Solute Concentration of the Primary Crystal

Fig. 2 presents four cooling curves with various degrees of undercooling respectively, one of which is the maximum undercooling of 138°C obtained in this experiment. Here, a slight difference was found between the deviation from the equilibrium eutectic temperature and that from the equilibrium eutectic temperature when solidified with undercooling. The average cooling rate prior to solidification was about 23°C/sec in the case of 8°C. Similarly, the average cooling rate was about 53°C/sec at 138°C.

Fig. 3 shows the relation between the degree of undercooling and the average solute concentration of the primary crystal solidified with undercooling. The movement of the solute concentration with the increasing degree of undercooling is also demonstrated in the equilibrium phase diagram of Al–Cu alloy. In view of this, the solute concentration of the primary crystal solidified with undercooling was nearly consistent with that of the solidus line in the equilibrium phase diagram when undercooled by less than 15°C. However, when the degree of undercooling increased over 15°C, the solute concentration, which was lower than was expected from the equilibrium solidus line, was increased

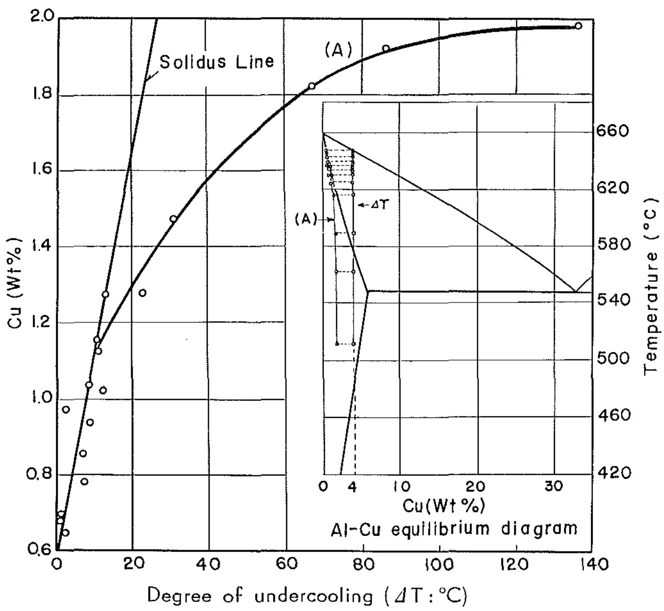


Fig. 3. Relation between solute concentration of the primary crystal and degree of liquidus undercooling in Al–4 wt. % Cu alloy.

to a saturated value of approximately 2 wt. % Cu. The distribution coefficient on such nonequilibrium solidification implies that the segregation tends to decrease with increasing undercooling.

3.2 The Change of Solidified Structure with Undercooling

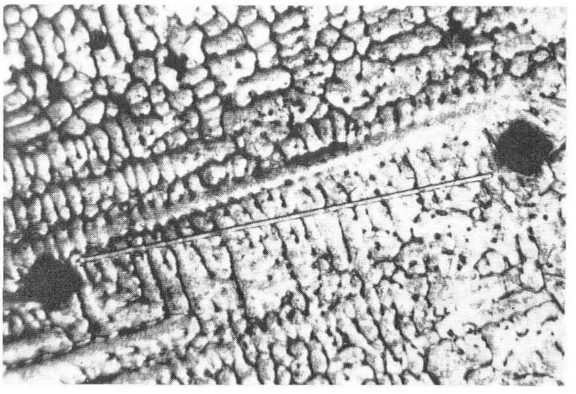
Generally, dendrite morphology is clearly observed within a range of small undercooling, where the solute concentration of the primary crystal increased corresponding to that of the equilibrium solidus line with increasing undercooling. As an example, Photo. 1-(a) shows the microstructure undercooled by 8°C. The straight line between two black points is a trace of the electron beam. The average distance of the dendrite arm was 30 μ.

Photo. 1-(b) shows the microstructure undercooled by 31°C, in which the dendrite became finer. The distance of the dendrite arm decreased below 20 μ. Thus, the enriched region of solute between the main stems of dendrite (or their arms) was subdivided.

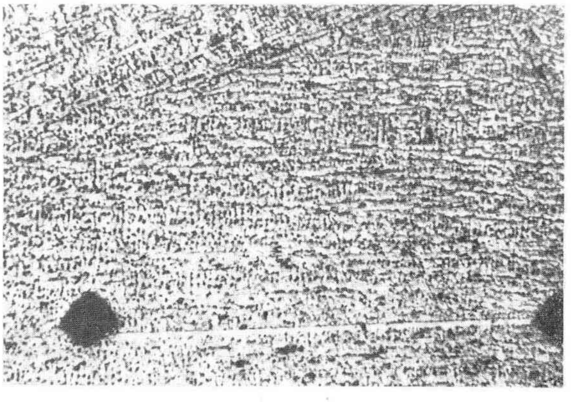
It was found from further microscopic observation that the quantity of eutectic crystals which existed in the interdendritic arm spacing was decreased in the structure undercooled by 31°C as compared with the structure undercooled by 15°C, and when undercooled by 31°C, θ phases appeared not only on the grain boundaries but also in the grains.

Photo. 1-(c) shows a microstructure with a maximum degree of undercooling of 138°C obtained by this experiment. The structure, in which eutectic was not observed, showed no dendrite morphology but clear subgrain boundaries and spherical θ phases 6 μ in dia. which were almost homogeneously distributed.

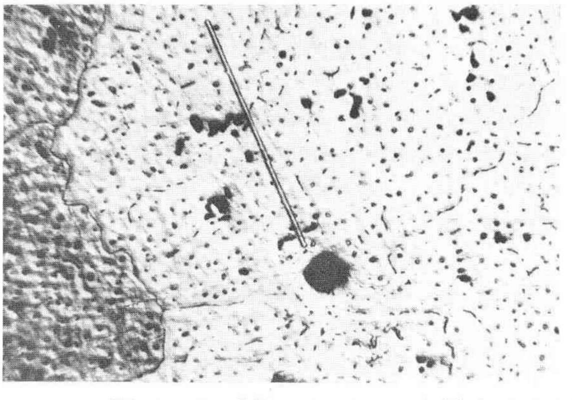
From the above microscopic observation, when the degree of undercooling increased over 15°C, eutectic and θ phase were observed, although the solute concentration was gradually increased. When undercooled further, the quantity of eutectic crystals was decreased and θ phase was increased. In the stage of the maximum undercooling of this experiment, no dendrite or eutectic crystal was observed. The structure showed clear subgrain boundaries and larger spherical θ phases which were almost homogeneously distributed on the grain boundaries and in the grains. The matrix in Photo. 1-(c) showed a constant solute concentration distribution except for θ phases, grain boundaries and their neighbourhoods. This concentration was about 2 wt. % Cu. This may be regarded as the saturated value, considering that the solute concentration of the primary crystal tends to increase with increased undercooling, while the equilibrium solute concentration is 0.64 wt. % Cu for Al-4 wt. % Cu alloy. It was then expected that the solute concentration would deviate from that of the equilibrium solidus line by precipitation of θ phases.



(a) $\Delta T = 8°C$; usual dendritic structure



(b) $\Delta T = 31°C$; fine dendritic structure



(c) $\Delta T = 138°C$; structure with clear subgrain boundaries and spherical θ phases

Photo. 1. Microstructures of Al-4 wt. % Cu small ingots solidified with various degrees of liquidus undercooling (ΔT) of 8°C, 31°C and 138°C respectively. $\times 40$

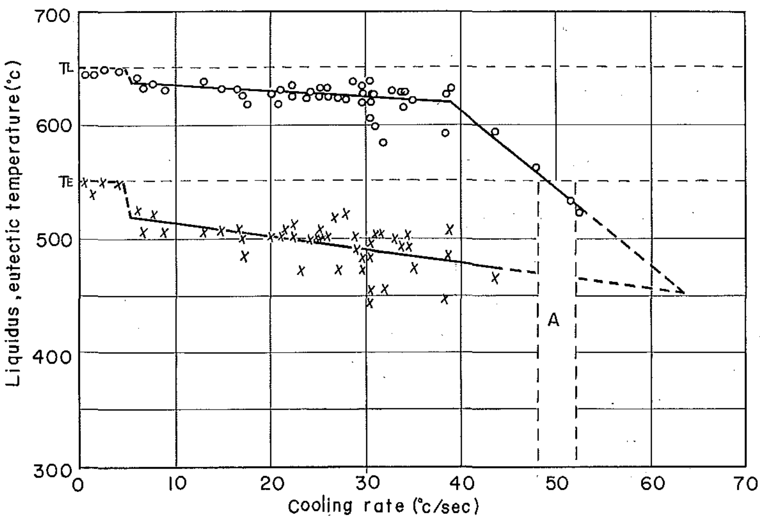


Fig. 4. Relation between degree of liquidus or eutectic undercooling and cooling rate.

T_L : Liquidus temperature of equilibrium solidification in Al-4 wt. % Cu alloy

T_E : Eutectic temperature of equilibrium solidification in Al-4 wt. % Cu alloy

A : Transitional range from dendrite structure to structures solidified with clear subgrain boundaries and spherical θ phases

3.3 Cooling Rate and Nonequilibrium Liquidus and Eutectic Temperatures

Figs. 2 and 4 show the change of nonequibrium liquidus and eutectic temperatures with increasing cooling rate. Each of these remained at a temperature closely corresponding to the equilibrium temperature when cooled to less than 6°C. However, as the cooling rate increased over 6°C, the liquidus and eutectic temperatures were gradually decreased. For example, the liquidus and eutectic temperatures had lower values of about 50°C and 70°C respectively from each equilibrium temperature at the cooling rate of 43°C/sec. Thus the deviation of eutectic temperature from the equilibrium eutectic temperature with the increasing cooling rate was rather large as compared with that of the liquidus temperature. When the cooling rate increased further, the liquidus temperature was rapidly decreased; at a cooling rate of about 50°C/sec the structure changed as described above from dendrite morphology to a structure with clear subgrain boundaries which was similar to solid solution morphology. This transition occurred when the primary crystal was undercooled below the equilibrium eutectic temperature. The temperature was about 450°C at the intersection of liquidus and eutectic lines in the rapid cooling region as shown in Fig. 4. This value may be regarded as the lowest temperature without solidification for Al–4 wt. % Cu alloy. The maximum degree of undercooling would be about 198°C. In addition, it has been previously reported that the maximum degree of undercooling in pure aluminium was about 195°C[3].

3. 4 Various Factors in Undercooling

In considering the actual condition of solidification it was expected that crystallization would be controlled by such experimental conditions as the surrounding atmosphere, mold surface, cooling method etc. rather than the action of nuclei contained in the molten metal. Thus it was shown that crystallization depended upon the physical properties and condition of the mold.

For example, when a molten aluminum sample 0.5 cm in radius was cooled at 50°C/sec, the temperature difference between the centre and surface of the molten metal was calculated at 8.5°C using the equation of heat conduction. In other words, the chilled surface was about 8.5°C lower than the centre of melt. The temperature difference between the centre and surface of the molten metal became larger when the radius of melt increased under the same condition or when the cooling rate alone increased. It was thus surmized that crystallization at the surface layer of a molten ingot became easier if the action of heterogeneous nuclei was based upon the same conditions.

Recently a method of slag treatment with the exception of quenching has been studied in the bulk specimens of metals and alloys[2)4)5)]. The slag acts to decrease various factors of nucleation at the inside and outside of a molten alloy; namely the slag would make nucleants adsorb on the surface of slag and change them into inactivated substances and also cause a stable film to be formed between the inside wall of the crucible and the surface of the molten alloy. The reason why Ni, Fe and Co are comparatively easy to undercool is that oxide films and inclusions would act generally as melted nucleants because of the high melting points of these metals. In relation to these phenomena a recent report[6] presenting experiments and theory for saturated solutions of urea and ammonium sulfate had it that, when a solid existed in a molten ingot, crystallization was promoted, since the melt was locally supersaturated in the neighbourhood of the solid surface by the interaction between molecules.

Various factors on crystallization were considered as described above. Next an investigation as to how the surface layer of molten alloy would be influence on undercooling was made. Firstly a molten Al–4 wt. % Cu alloy weighing 70 g was solidified by air cooling in a graphite crucible with an inside dia. of

30 mm. The specimen was suspended and held for 5 hr. and 20 hr. respectively in an air bath at 550°C in order to oxidize the surface. Such specimens were again placed into the graphite crucible in such a way that the condition of surface layer was not disturbed. The degree of the surface oxidation, which would be influence on undercooling, was examined next.

As a result it was shown that the melting-solidification cycles was a suitable means to determine the influence of surface oxidation. Fig. 5 shows the results. In a specimen with no previous treatment of surface oxidation, the degree of undercooling remained constant at about 3.5°C at less than 32 cycles. However, the number of melting-solidification cycles increased to more than

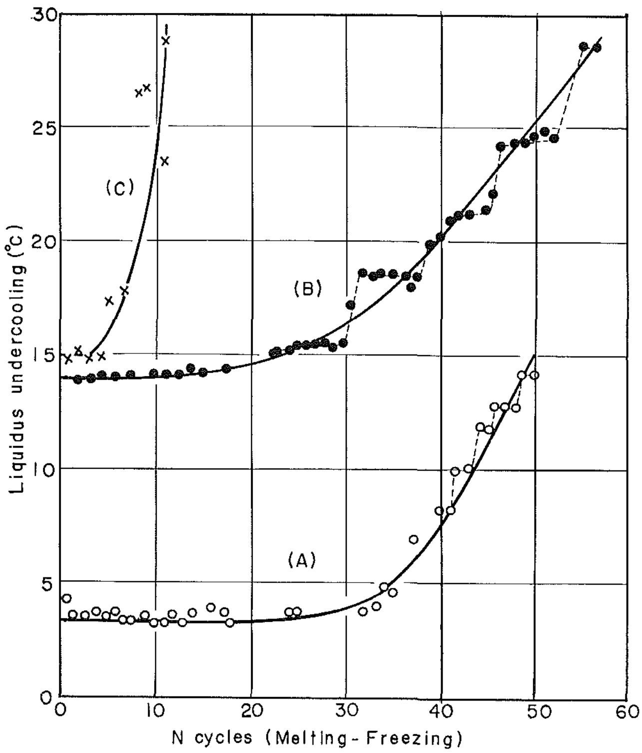


Fig. 5. Relation between degree of liquidus undercooling and cycle number (N) of melting-freezing in Al–4 wt. % Cu alloy. (30 mm ϕ : Graphite crucible)
A : Non-oxidized sample
B : Pre-oxidized sample at 550°C for 5 hr. under air
C : Pre-oxidized sample at 550°C for 20 hr. under air
Dash lines show that the degree of undercooling is increased stepwise with the increasing number of melting-solidification cycles.

32, and the degree of undercooling was rather rapidly increased. On the other hand, the specimen with surface oxidation was considerably undercooled from the beginning of melting-solidification cycles. The degree of undercooling of the oxidized specimen was gradually increased from 20 cycles in the case of holding for 5 hr. at 550°C, while it was rapidly increased from 4 cycles for 20 hr. at 550°C. It was thus considered that a stable layer was formed between the inside wall of the crucible and the ingot surface. And moreover, the degree of undercooling tended to increase stepwise with the increasing number of melting-solidification cycles as shown by dashed lines in Fig. 5. It was expected that nucleants in a molten alloy would be gradually carried to the surface of the melt or dissociated in the process of melting-solidification cycles. In fact the degree of undercooling was increased stepwise with a small number of melting-solidification cycles after an appropriate number of cycles of it. It was expected that this would occur because nucleants in a molten alloy become unstable with the increasing number of melting-solidification cycles, and the number of nucleants would then be decreased. It was considered that the study on these phenomena would lead to an explanation of the mechanism of heterogeneous nucleation and the effect of slag treatment.

4. Conclusions

Undercooling phenomena were studied in bulk specimens of an Al–4 wt. Cu alloy cooled by spraying water onto a graphite crucible.

1) The solute concentration of the primary crystal solidified with undercooling was almost consistent with that of the solidus line in the equilibrium phase diagram when undercooled by less than 15°C. However, when the degree of undercooling increased over 15°C, the solute concentration was increased to a saturated value of approximately 2 wt. % Cu showing a deviation from that of the equilibrium solidus line. Such a deviation of solute concentration from the solidus line was expected to be caused by precipitation of θ phase.

2) The dendritic structure of specimens solidified with undercooling became finer with the increasing degree of undercooling. When the primary crystal was undercooled below the equilibrium eutectic temperature, the microstructure was not dendritic. The structure showed clear subgrain boundaries and spherical θ phases which were homogeneously distributed not only on the grain boundaries but also in the grains.

3) It was suggested from the change of nonequilibrium liquidus and eutectic temperatures with increasing cooling rate that the maximum degree of undercooling expected in Al–4 wt. % Cu alloy would be about 198°C.

4) When melting and solidification were alternately repeated many times on one specimen, the degree of undercooling was increased stepwise with the increasing number of melting-solidification cycles. Also it was found that the oxidation of a specimen surface before melting increased the degree of undercooling.

Acknowledgement

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