JOURNAL OF MATERIALS SCIENCE 3 (1968) 139–149

Origin of the Equiaxed Zone in Small Ingots

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Received 23 October 1967

It is deduced by thermal analysis that no entirely new crystals are nucleated in the interior of an ingot at any time after pouring. By comparing the conditions for columnar growth in ingots and in unidirectional solidification experiments, it is concluded that in the ingot, sufficient constitutional supercooling for nucleation might occur if it were not prevented by the presence of crystals in the liquid.

At low pouring temperatures, most of the equiaxed grains are nucleated as separate crystals at the time of pouring. When the superheat is higher, the main process for the origin of the equiaxed zone appears to be a multiplication mechanism operating by local remelting. Dynamic procedures used during unidirectional solidification and conventional ingot freezing permit one to conclude that the main mechanism operating to refine the equiaxed structure, as a function of imposed disturbances (mechanical or forced fluid flow) is a multiplication mechanism, most likely the process of detachment of dendritic arms by remelting.

1. Introduction

It has been long recognised that the crystals or grains in an ingot are of two distinct shapes, described as columnar and equiaxed. A columnar crystal has one dimension many times greater than the others. This long dimension is in, or close to, the direction of heat flow in the solidifying metal. In the equiaxed grains, the three dimensions are comparable. The small equiaxed crystals, often found at the surface which has been in contact with the mould wall, are known as chill crystals and are believed to nucleate in the part of the melt which is rapidly cooled by contact with the mould*.

Some of these grains grow inwards to form the columnar zone. It was shown by Walton and Chalmers [1] that, in the competitive growth process in which some of the chill crystals are suppressed by others which become columnar grains, the most favoured grains are close to particular orientations; this is the origin of the preferred orientation often found in the columnar zone of ingots. The origin of the equiaxed zone in the interior has, on the other hand, not been so evident. It was first proposed by Winegard and Chalmers [2] that the equiaxed grains nucleate, after the columnar zone has formed, as a result of the constitutional supercooling of the remaining liquid. The constitutional supercooling is caused by the rejection of solute at the advancing interface between the columnar crystals and the liquid. Chalmers [3] pointed out, however, that there were several objections to this early proposal, and that consideration should be given to the possibility that all the crystals, equiaxed as well as columnar, originate during the initial chilling of the part of the liquid in contact with the mould. In this regard, recent work by Cole and Bolling [4] has emphasised the importance of thermal convection in the columnar to equiaxed transition, and Jackson *et al* [5] have proposed that a

*Recently Bower and Flemings [6] purport to show that a "multiplication mechanism" is responsible for the formation of the chill zone. However, Biloni and Morando [7] find that the particular experimental conditions used by Bower and Flemings are not always applicable to conventional ingots, and further that the conventional nucleation mechanism is largely responsible for the formation of the chill zone when the alloy is cast in a graphite mould, as in the present case.

remelting phenomenon is responsible for the formation of the equiaxed region.

The purpose of this paper is to present a series of experimental results relating thermal analysis and metallographic structures when different geometric, thermal and dynamic conditions are imposed. The results are discussed in connexion with the different mechanisms just mentioned.

2. Experimental Techniques and Results

Most of the experiments were made with aluminium (99.993% purity) and aluminium/copper alloys with 0.5 to 10.0 wt % of copper. The copper used was 99.999% pure. Some experiments were also made with Sn/Pb alloys with 1.0 to 10.0 wt % of lead. The purity of both metals was 99.999%.

The metallographic observations on Al/Cu alloys were made on sections of the small ingots used in our study, by two metallographic techniques. (i) The Lacombe-Biloni film technique, which reveals in a semiquantitative way the distribution of solute on a scale limited only by the resolution of the optical microscope; this method has previously been used to study the "predendritic" stage of solidification [8], that is, the part of any crystal that grew before the dendritic structure developed. (ii) A second method was to use the Disa Electropol. The sample, after a 600 grinding paper, is electrolytically polished for 50 to 60 sec in the standard solution at a current density of 1.5 A/cm^2. It is then electrolytically etched in the same electrolyte at 0.15 A/cm^2 for 8 sec. The results obtained with this technique were similar to those of the other, with the advantage of more rapid preparation. To avoid misinterpretation in the detection of the predendritic areas, the regions where they appear were observed on three mutually perpendicular planes.

2.1. Thermal Analysis

Thermal measurements were made in order to determine the time/temperature relationship at various locations, under various cooling conditions. All the observations were made with 38 gauge chromel/alumel thermocouples sheathed in alumina except at the tip, connected to a two-channel Leeds Northrup Speedomax recorder. The following observations were made. (i) The Al/Cu alloy was allowed to cool in a graphite mould in which it had been melted. It was found that nucleation always took place when the supercooling reached a value of between 1 and 2.5° C, in agreement with the results of Kohn and Philibert [9]. Similar results were found when the melting and cooling took place in an alumina mould. It was concluded that this range of supercooling is a characteristic of the alloy under the particular experimental conditions: crucible, material, and purity of the metals used. The form of the cooling curve is in agreement with the results of Kohn and Philibert [9], and the most important feature is the existence of a long plateau that corresponds to a major part of the solidification process. The plateau appears after recalescence is complete.

The variation in the shape of the curves with the amount of solute has already been discussed by Kohn and Philibert. However, we shall emphasise one important aspect of the freezing process which can be detected by the thermal analysis. Fig. 1 corresponds to cooling curves of Sn and three Sn/Pb alloys. The thermocouple was situated near the bottom of an alumina crucible of about 150 cm^3. After the first abrupt rise, these curves show that the rate at which the temperature rises toward the plateau value decreased with increasing solute content. We explain this on the basis that the rate of growth of crystals in the alloy melt is limited by the diffusion of solute from solute-rich regions, rather than by the conduction of latent heat, as for a pure metal. The relatively slow growth that takes place under diffusion produces a correspondingly slow rate of evolution of latent heat, and therefore, a slow approach to the plateau temperature, which is the temperature of steady state growth of the dendritic crystals under the prevailing heat extraction conditions.

(ii) Molten Al/Cu alloy was poured into a cold graphite mould. The mould dimensions were: 8 cm ID; 10 cm OD; 12 cm height. One thermocouple (A) was placed 1 cm from the bottom of the crucible and another (B) near the centre of the mould, i.e. 4 cm from the bottom and lateral walls.

Results of such tests are shown in figs. 2 and 3. The pouring temperatures were 25, 30, 35, and 40 (in fig. 2), and 60 and 70° C (in fig. 3) above the liquidus temperature. In each case, the thermocouples were simply compared by placing them together (moving up the thermocouple (A) for the last part of the solidification process) and the differences between the read-

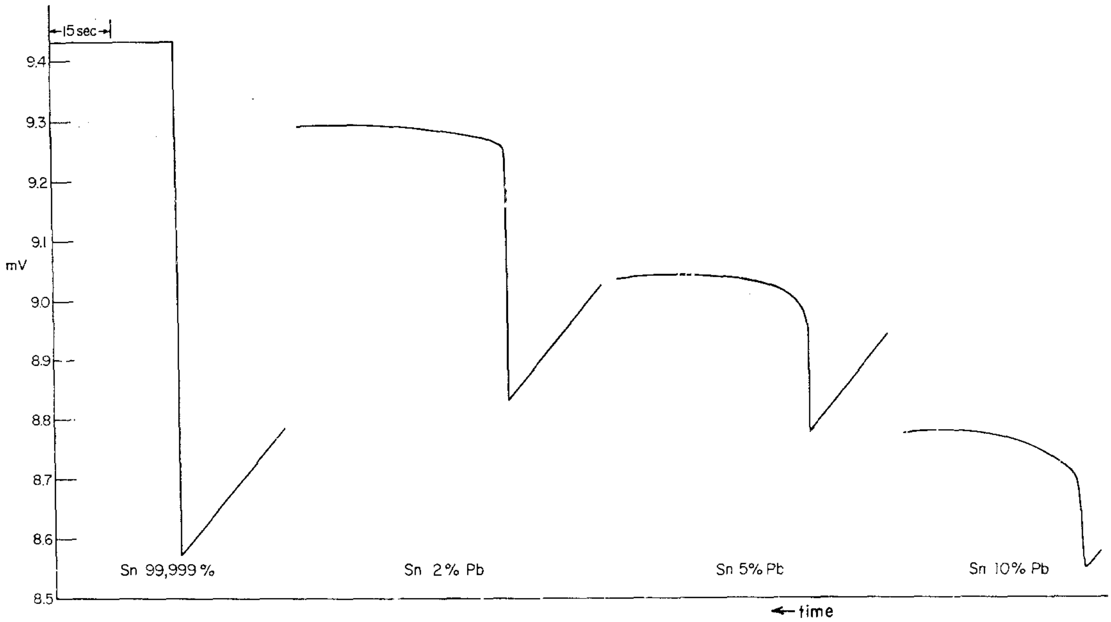


Figure 1 Freezing curves for Sn of 99.999% purity and Sn/Pb alloys.

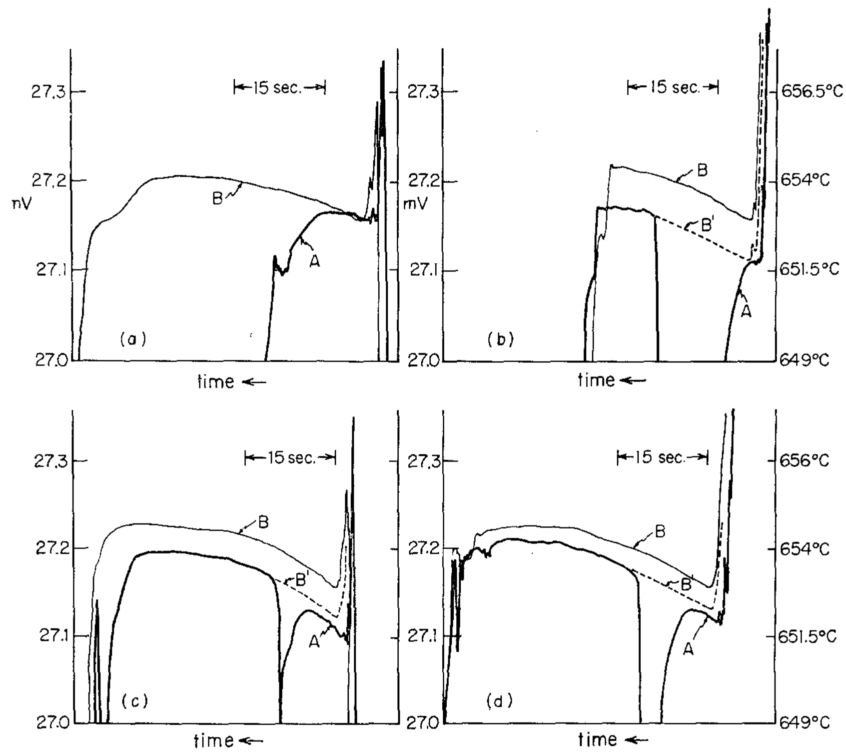


Figure 2 Four different freezing curves in the case of Al/2% Cu alloy poured with superheat of 25, 30, 35, and 40° C (a-d). The curves B′ are corrected for the difference in thermocouple readings when they were placed together.

ings (0.5° C in the case of fig. 2b) were used to correct the readings, giving the curves labelled B′ (the curve actually recorded being B). The curves that would be obtained with identical thermocouples are thus A and B′. Recalibration against aluminium of 99.999% purity showed a similar difference in the temperature readings.

The pouring superheats were from 120 to 20° C, selected to produce macrostructures ranging from completely columnar to completely equiaxed [3]. The results could be divided into two different classes. When the pouring temperature was so low that the columnar zone was suppressed, the curves were of the type shown in fig. 2a-d. The corrected curves show that the nucleation temperature is the same at both thermocouples within experimental error, and is reached at almost the same time. However, the later parts of the curve are quite different. While in one cooling curve, the temperature drops after several seconds, the other curve shows a slow rise in temperature until a plateau is reached. After remaining for several seconds at this level, the temperature drops very rapidly as observed in the Kohn and Philibert type of experiments [9]. This condition arises when the superheat is less than 40 to 50° C.

Above this temperature range, a well developed columnar zone is formed and the cooling curves are of the type shown in fig. 3a-d. There is very little recalescence, but the difference in the plateau levels is about 1° C. It may be seen that the thermocouple at the centre reaches the plateau about 3 to 5 sec after the outer thermocouple. Fig. 4a-d shows the structure as a function of the amount of superheat.

Special attention was paid to the metallographic aspects of the sub-structure in the different parts of the structure to detect the predendritic areas [8]. The equiaxed region contains a considerable number of predendritic areas, each of which is the origin of one grain. The columnar region consists largely of cellular dendritic sub-structure. However, while most of the grains can be traced back to the chill zone, there are some which cannot. Similarly, it is often possible to find grains *included* in the columnar zone but differing from it in orientation to such an extent that growth was suppressed in the same way as the "unsuccessful" grains of the chill zone [8].

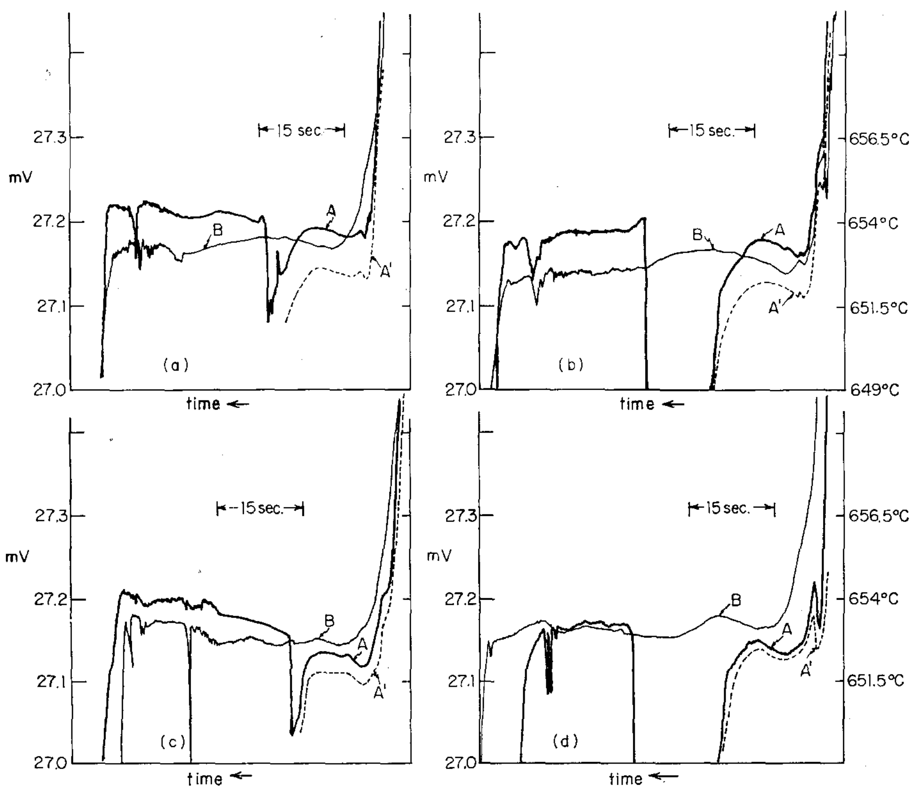


Figure 3 (a) and (b) correspond to 60° C superheating; (c) and (d) to 70° C superheat. The oscillations in the curves at the left correspond to the agitation of the thermocouples close to one another to assure the measurement of the same temperature. In this case curve A was corrected to A′.

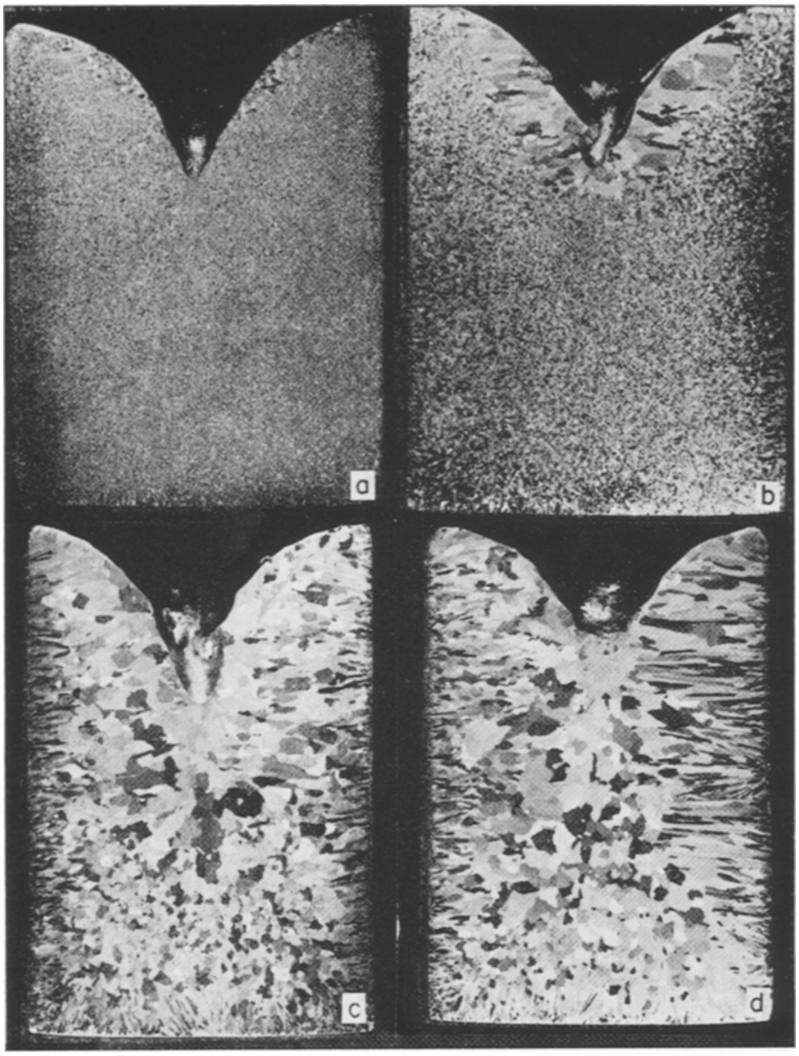


Figure 4 Macrostructures in Al/2% Cu ingots poured with different superheat; (a) 20° C, (b) 35° C, (c) 50° C, (d) 65° C.

2.2. Unidirectional Experiments

Plaskett and Winegard [10] studied unidirectional (upward) solidification in which both the temperature gradient in the liquid (G) and the rate of advance of the interface (R) were controlled. The liquid was undisturbed. In these experiments either a columnar or columnar plus coarse equiaxed zones can be produced by unidirectional solidification. These results were confirmed and complemented by the use of a similar apparatus, for which the conditions are controlled so that the value of the parameter $G/R^{\frac{1}{2}}$ decreases continuously and can be calculated for the conditions where the structure changes. These experiments were of two kinds.

(i) The determination of the transition from a columnar to an equiaxed structure. In our case, the initial value of $G/R^{\frac{1}{2}}$ for each value of C_0 was much less than in the experiments of Plaskett and Winegard on Al/Mg alloys [10]*.

When a thermocouple was situated in a columnar region, no supercooling was detected. On the other hand, when the thermocouple was situated in a region which becomes equiaxed, supercooling between 1 to 2° C, followed by recalescence, was detected. In either case,

*Cole and Bolling [11] have found that the columnar to equiaxed transition for the Plaskett and Winegard type of experiments can change even with minor differences in purity of the alloy.

precautions were taken to avoid lateral loss of heat, and in our experiments no evidence was found of nucleation induced by the thermocouple itself, as reported by Plaskett and Winegard.

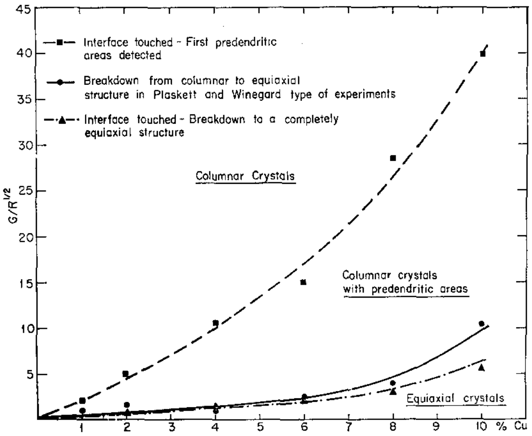


Figure 5 Relationship between $G/R^{\frac{1}{2}}$ and C_0 in the case of Al/Cu; (i) breakdown from a columnar to an equiaxed region (Plaskett and Winegard type experiments); (ii) survival of the first predendritic areas when the solid/liquid interface is mechanically disturbed; and (iii) breakdown from a columnar region to a *completely* equiaxed structure when the interface is mechanically disturbed.

(ii) The solid/liquid interface was disturbed mechanically every minute after the beginning of solidification by a 1 mm diameter stainless steel rod preheated to the liquidus temperature of the alloy. Similar results were obtained with an alumina rod. In each case, the rod was moved so that it gently touched the interface. When $G/R^{\frac{1}{2}}$ had fallen below some critical value, each alloy had fine equiaxed grains with predendritic sub-structure in the regions where the interface was disturbed. Another critical value of $G/R^{\frac{1}{2}}$ corresponded to the complete transition from a columnar to a fully equiaxed structure. These values are very close to those found for the presence of equiaxed grains in the undisturbed cases, but the grain size is much smaller. Fig. 5 shows the relationship between $G/R^{\frac{1}{2}}$ and C_0 for the Plaskett and Winegard type of experiments, the conditions for the survival of equiaxed grains in front of the interface, and the transition from columnar to completely equiaxed regions after mechanical disturbance of the interface. Fig. 6 shows (with an arrow) the regions in Al/6% Cu samples where equiaxed grains appear after mechanical disturbance of the interface and, with *two* arrows, the transition from columnar to a fully equiaxed structure. The difference of grain size between these two samples is noticeable. In the same figure, an Al/0·5% Cu alloy grown with very low temperature gradient shows, as expected, that equiaxed crystals appear after every mechanical disturbance, but that there is no breakdown from a columnar to a "real" equiaxed region (see fig. 5).

Fig. 7 shows an example, at larger magnification, of the detailed structure in the region where grains survive in front of the interface.

2.3. Effect of Dynamic Conditions Upon the Structure of the Ingot

The effect of liquid motion and mechanical disturbance of the interface on the structure were studied in conventional ingots of aluminium of 99.993% purity, and Al/2 wt % Cu under the following different experimental conditions.

(i) By bubbling preheated He: (a) from the beginning of the solidification process; (b) after the solidification started.

(ii) Mechanical disturbance of the interface in the same way as in the unidirectional experiments.

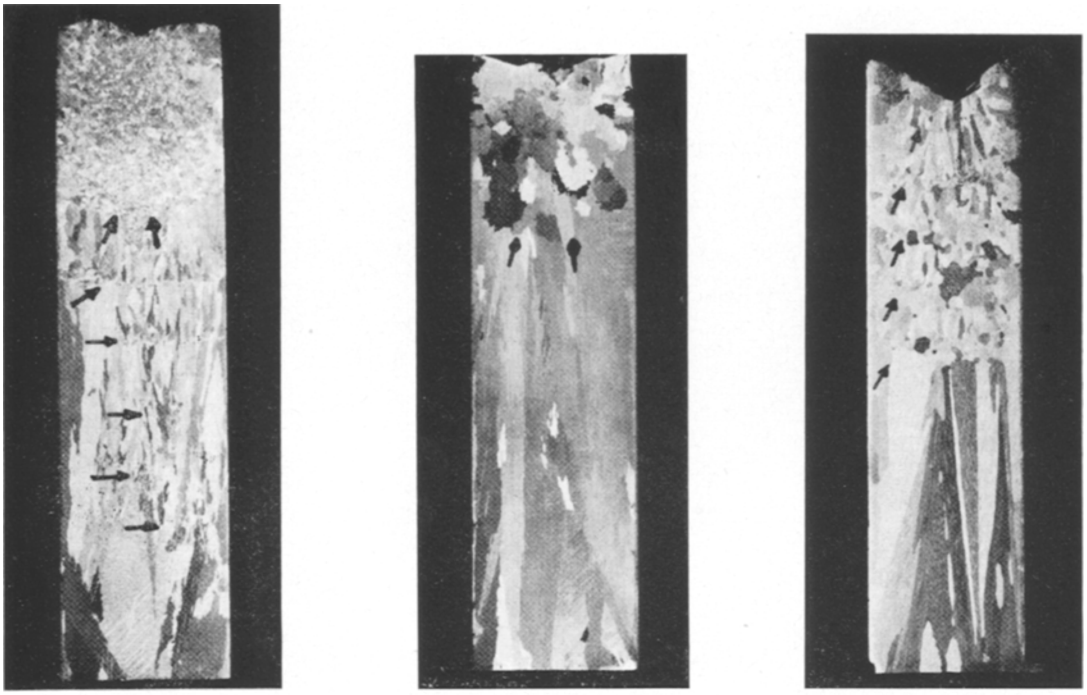
(ii) By stirring of the liquid with a preheated rod of alumina after the solidification started. These experiments were carried out on: (a) ingots cast in cold graphite moulds and (b) ingots melted in graphite moulds and subsequently cooled in air. Fig. 8a-h provides the representative structures obtained. The results can be set forth as follows.

Al/2 wt % Cu alloys If the bubbling of He or mechanical stirring was operated from the beginning of the solidification process, the effect upon the structure was to produce a shorter columnar zone and a much finer equiaxed zone, fig. 8a, b.

When the dynamic condition, whichever it was, began to operate after the solidification process the effect upon the structure was a direct function of the degree of the disturbance, see fig. 8c-f.

The refinement of the structure (i.e. the appearance of a fine equiaxed structure) arises both when the ingots are cast in cold moulds, or melted and frozen in the same mould where there is not a chilling effect (fig. 8g).

The transition from the columnar to the equiaxed structure is sharper under disturbance



(a) (b) (c)

Figure 6 (a) Al/6% Cu alloy grown unidirectionally and mechanically disturbed every minute. Single arrows show times at which the interface was disturbed, and the *two* arrows show the beginning of a completely equiaxed structure. (b) Breakdown from columnar to equiaxed structure in Al/6% Cu alloy in the case of Plaskett and Winegard type experiments. (c) Al/0.5% Cu alloy grown with low values of $G/R^{\frac{1}{2}}$. Equiaxed grains appear after each disturbance.

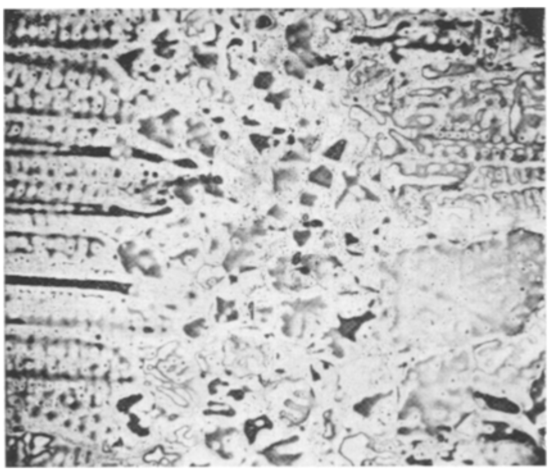


Figure 7 Al/2% Cu alloy grown unidirectionally from left to right and disturbed mechanically; predendritic areas in front of the interface after disturbance. Disa-Electropol polished and etched.

than in the case of conventional ingots. The sub-structure is predominantly similar to that termed predendritic with an appearance similar to the central part of the sub-structure shown in fig. 7.

Al of 99.993%*purity* The application of dynamic conditions forces the appearance of a large number of areas again similar to those termed predendritic (fig. 8h). The grains of the central part of the ingot are much smaller in size but are always columnar. Fig. 9 has been included in order to show the finer columnar region of the ingot of fig. 8h. The anodic film technique which could be used here permitted detection of the segregation pattern and consequently the origin of the grains.

3. Discussion

The experimental evidence presented shows that, under the conditions of our ingot experiments on Al/Cu alloys, nucleation of entirely new grains takes place only at the time of pouring and not at some later time as envisaged in the Winegard and Chalmers theory [2]. (It is confirmed in section B, however, that the geometry can be modified so that nucleation can occur as a result of constitutional super-

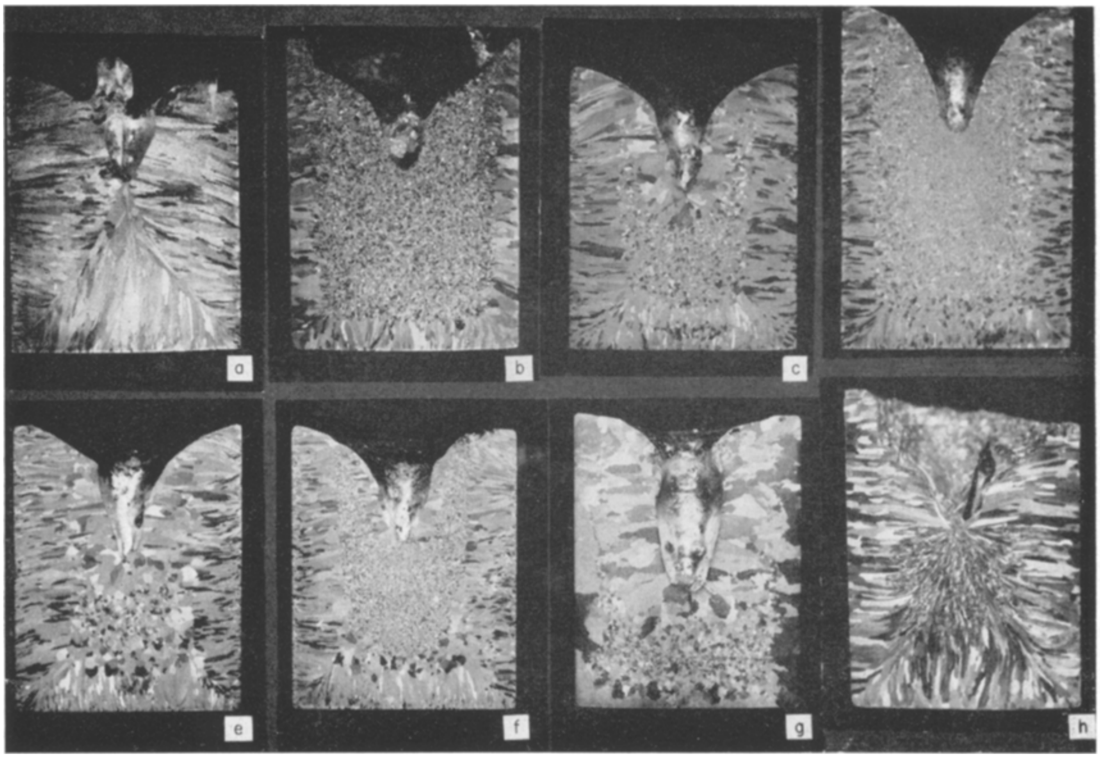


Figure 8 (a-g) Al/2% Cu alloys; (h) Al of 99.993% purity. (a-f) correspond to alloys poured with 110° C superheat; (g) to an alloy melted and frozen in the same mould; (h) to Al of 99.993% purity poured with 30° C superheat. The ingots were treated as follows: (a) conventional ingot; (b) bubbling of He preheated from moment of pouring; (c) interface mechanically disturbed after 10 sec of the initiation of the solidification process; (d) interface disturbed after every 10 sec; (e) liquid mechanically stirred during 2 sec after 10 sec of initiating the solidification process; (f) liquid mechanically stirred during 10 sec after 10 sec of the initiation of the solidification process; (g) liquid mechanically stirred during 10 sec after 30 sec of the initiation of the solidification process; (h) bubbling of He from the moment of pouring.

cooling, as proposed by Winegard and Chalmers [2], and observed experimentally by Plaskett and Winegard [10].) The experiments reported show that nucleation caused in this way is always accompanied by a characteristic thermal curve which is obtained (in small ingots) only during the initial period when the metal is entering the mould. During this period, some of the metal is supercooled sufficiently for nucleation to occur. The thickness of the layer of liquid in which this occurs depends on the pouring temperature and the thermal properties of the mould. If the rate of heat extraction is high and the pouring temperature is low, a relatively large volume of the liquid can be supercooled; in most extreme case of chill casting, nucleation takes place throughout the melt and a completely equiaxed structure is obtained. The nucleation temperature, according to the thermocouple traces, is reached at practically the same time at the centre and near the bottom of the mould. Because the rate of extraction is high near the wall, and the evolution of latent heat is clearly limited by diffusion of solute in front of the interface, under these conditions the temperature near the walls falls very quickly. The long recalescence period may thus be an indication of predendritic growth. At the other extreme (high superheat) nucleation occurs in only a small fraction of the liquid. When the considerations about the thermocouple near the wall given in the previous case are applied in this case, the absence of recalescence at the central thermocouple seems to be a proof that no nucleation occurs at this region of the liquid. In neither case is there any thermal evidence for nucleation at any time later than that of the initial cooling of the liquid.

Our conclusion, based on the experiments described above, is therefore, that nucleation

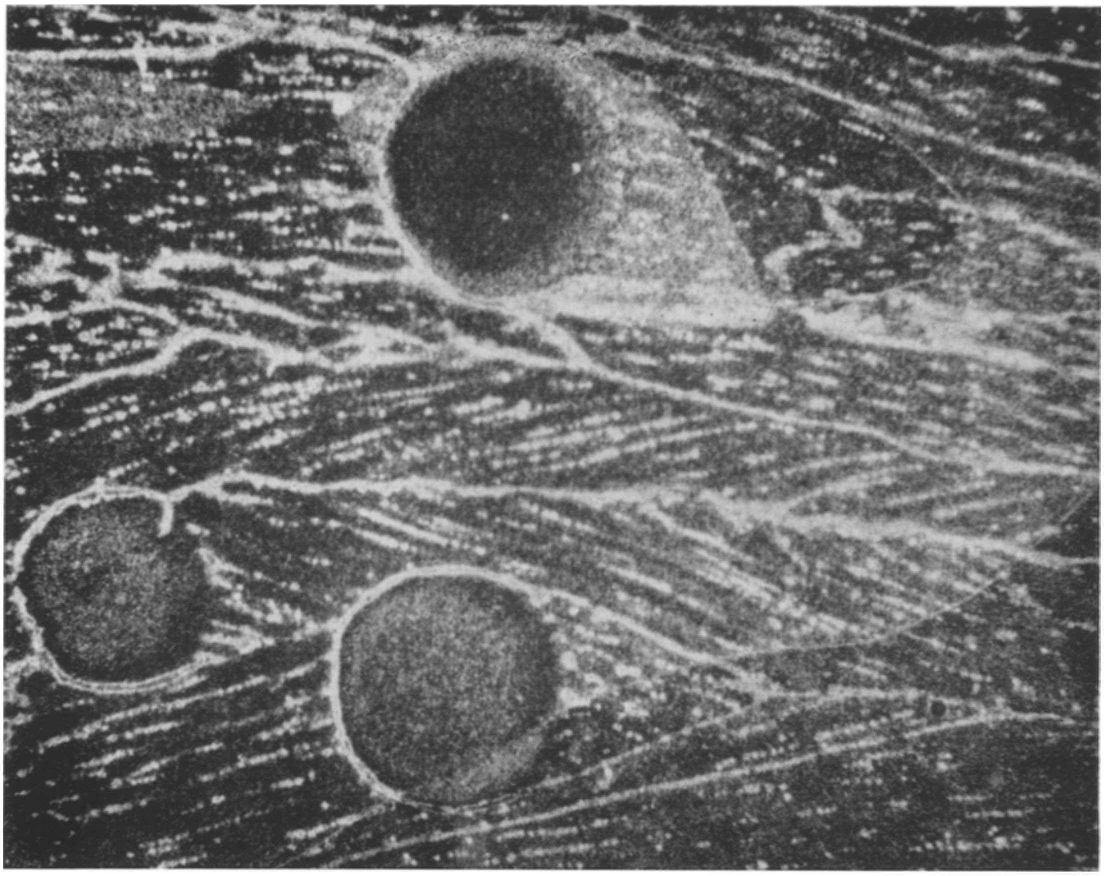


Figure 9 Metallographic sub-structure of the centre of the ingot of fig. 8h. Anodic film technique.

occurs only at the time of pouring; but this leaves unanswered the question of whether the equiaxed grains originated as separate crystals at the time of pouring, or whether they arose later, as fragments of columnar grains.

The following observations must be explained by any answer to this later question. (i) The unidirectional experiments suggest that a minimum value of $G/R^{\frac{1}{2}}$ seems to be necessary for the survival of predendritic regions created by mechanical action in a narrow region in front of the interface. In the same way the breakdown to a completely equiaxed structure presents essentially the same value of $G/R^{\frac{1}{2}}$ for both types of unidirectional experiments.

(ii) The sub-structure morphology of the grains in different types of experiments (conventional ingots free from, or under, dynamic conditions, and unidirectional ingots mechanically disturbed) present the same characteristics: predendritic areas that break down to a cellular dendritic substructure with a growth direction opposite to that of the flow of heat. From the metallographic point of view, it is not possible to differentiate the predendritic areas which grew from a nucleation mechanism [3] from the predendritic areas which grew from detached dendritic arms through a multiplication mechanism [5] and thus we do not choose a new name for the latter type*. In any case the crystals will

*Recently Southin [12] in discussing the equiaxed zone as well as the sub-structure of those columnar grains with a similar, i.e. predendritic sub-structure, chose to use the term "head of comet grains". Southin affirms that this structure has a "dendritic characteristic". However, this may be a conflict in terms. We define a dendrite as a linear, branched sub-structure of which the arms are all parallel to major crystallographic directions [13]. The development of this characteristic may depend on the amount of constitutional supercooling present in the liquid. In the case of aluminium of 99.993% purity, where the amount of constitutional supercooling is necessarily low, the crystal may not develop arms (see fig. 9).

grow in a slightly supercooled medium as an irregular predendritic region [8] until the main solid reaches them.

We propose the following sequence of events. (i) At low superheat the liquid is rapidly cooled by contact with the mould, to a temperature at which nucleation occurs on the most effective nucleant particle available. The volume of liquid that is cooled to this extent increases with decreasing pouring temperature. Below some critical range of temperature, all the liquid is supercooled to an extent that allows nucleation.

The results of Uhlmann *et al* [14], and Cole and Bolling [15] support the results presented here. That the damping of convection at very low superheat by magnetic fields or rotation does not eliminate the equiaxed structure is especially significant.

(ii) By increasing the superheat, the volume of liquid that is cooled to the nucleation temperature is reduced. As already stated, this is shown by the fact that the thermocouple situated at the centre does not show recalescence. The nuclei formed in contact with the mould grow rapidly because heat is extracted continuously by conduction into the mould wall. We suppose that other nuclei move with the liquid into the central regions of the mould, mixing rapidly with the hotter liquid that has not been close enough to the wall to be substantially cooled. The 3 to 5 sec time delay for both thermocouples to reach the same temperature (see fig. 3) is a measure of the rate at which this takes place.

An important process by which the "hot" liquid is cooled during mixing is the heat it must supply to melt some of the crystals that have already formed. For aluminium, 1 g of liquid would be cooled 10° C by melting 0.05 g solid. Thus, if the pouring temperature is sufficiently high, the "floating" crystals melt completely. At lower temperature, some or most of these crystals (depending on the superheat) may survive the mixing process and remain in existence, growing as predendritic crystals in the liquid. When account is taken of our thermal analysis and the results presented by Uhlmann *et al* [14], and Cole and Bolling [15] at medium and high superheat, it seems most probable that with increase of the superheat, the number of grains that survive the mixing with the "hot" liquid is lower and therefore the remelting mechanism becomes more important [5]. The number of grains that come from the initial nucleation may change continuously with superheat, but we can only be sure that they survive when the superheat is less than that at which recalescence is detected by the central thermocouple. Above and below this critical temperature it appears logical to suspect a superposition of both mechanisms.

(iii) The floating crystals probably grow predendritically and each crystal is surrounded by its diffusion field of higher solute content, and therefore lower liquidus temperature, than the unaffected regions of the melt. After a time that may depend on the distance between the crystals and on the temperature of the melt, the diffusion fields of the growing crystals begin to impinge on each other. At this time, the growth of columnar crystals is interrupted and the extraction heat is such that a cellular dendritic sub-structure is developed [8, 12]. It is envisaged that an isolated predendritic crystal with its diffusion field can be "trapped" by the columnar zone [8] which grows around it, but the columnar zone does not grow between floating crystals whose diffusion fields (that have values above a critical minimum) have impinged. Figs. 8h and 9 support this thesis: the presence of numerous predendritic areas with very weak diffusion fields around them cannot produce an equiaxed structure, only a finer columnar region.

(iv) Regarding the effect of dynamic conditions upon the structure, the unidirectional type of experiments show that in convection-free systems, unless the constitutional supercooling criterion is met, the predendritic crystals created by mechanical action (through a multiplication mechanism) can survive only in a narrow region in front of the interface where they are protected from melting. The existence of this region corresponds to the existence of a minimum of constitutional supercooling that depends on a critical value of the parameter $G/R^{\frac{1}{2}}$. Similar results have been obtained by Wojciechowski and Chalmers [16] with unidirectional growth and forced fluid motion of the liquid in front of the interface.

In conventional ingots, any type of disturbance (mechanical or unforced fluid motion) causes a multiplication mechanism [5] to operate producing a "cloud" of crystals in the liquid. Any fluid motion, natural or forced, increases the heat transfer and thus the tendency to reach the necessary $G/R^{\frac{1}{2}}$ value for the survival of the dendrite fragments. The crystals created by this mechanism grow predendritically in the slightly supercooled liquid until they form a continuous diffusion field that stops the growth of the columnar grains. If the diffusion field is very weak, as in the case of aluminium of 99.993% purity, the result is a finer columnar zone.

4. Conclusions

In Al/Cu alloys under the conditions of our experiments, nucleation can be detected by thermal analysis as a recalescence of about 1.0 to 2.5° C. These observations lead to conclusions about the mechanisms involved in the origin of the equiaxed zone in ingots grown in different geometric conditions.

In the geometric condition of a convection free unidirectional system, the development of constitutionally supercooled liquid in front of the interface permits the formation of an equiaxed zone by heterogeneous nucleation.

In conventional laboratory ingots poured with low superheat, nucleation takes place all through the liquid and this produces a fine equiaxed structure. At higher superheats, it is not possible to affirm if the grains nucleated in the vicinity of the mould wall survive and form part of the equiaxed zone. Probably crystals arising from a multiplication mechanism constitute most of the equiaxed zone in the case. Thermal analysis permits the conclusion that the absence of recalescence at a thermocouple situated at the centre of an ingot, refutes the Chalmers and Winegard theory, under the geometric conditions of conventional ingots.

Different types of mechanical action or forced fluid motion enhance the columnar to equiaxed transition, probably through a remelting multiplication mechanism.

Acknowledgements

This work was supported in part by the Advanced Research Projects Agency under contract ARPA-SD-88, the United States Steel Corporation under contract 5208, and by the Division of Engineering and Applied Physics, Harvard University.

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