JOURNAL OF MATERIALS SCIENCE 5 (1970) 843-850

The Structure of High-Purity Copper Ingots Nucleated at Large Undercoolings

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The structures observed in small ingots of high-purity copper, nucleated at temperatures far below the melting point, have been studied. In contrast to other metals, no general recrystallisation is observed in high-purity copper even after nucleation 200° C below the melting temperature. The reasons for this are discussed and it is suggested that a dendrite arm re-melting process is a prerequisite for general recrystallisation. This requires a higher impurity content than the present copper ingots contained. Annealing treatments failed to produce a decrease in grain size despite the highly dislocated structure produced during freezing. The observed mechanisms of grain-boundary migration are discussed in terms of a recent theory by Gleiter, and confirm earlier evidence that many of the grains nucleated originally are in mutual twin orientation.

1. Introduction

When a liquid melt is cooled to a temperature far below its equilibrium melting temperature before nucleation of the solid phase occurs, solidification will proceed very rapidly from the nucleus [1] and the final structure of the cast ingot can be radically different from that of a similar melt solidified normally with a small undercooling. In alloyed materials, undercooling produces reductions in both the dendrite arm spacing and in the segregation ratio ($C_{\max}/C_{\min}$) across the dendrite arms, and can therefore result in a shortening of subsequent costly homogenisation anneals [2, 3]. In certain pure metals (Ag, Co, Ni) a large discontinuous decrease in the final grain size of ingots has been observed after undercoolings of 130 to 175° C [4-6]. The grain structure of these ingots was completely equiaxed and annealing twins were present. This structural refinement has consequently been attributed to spontaneous recrystallisation during or immediately after solidification.

Such a process is of course very desirable since it greatly reduces many of the deleterious characteristics of castings, such as directionality and impurity segregation to grain boundaries. Powell and Hogan [7] were unable to produce recrystallisation in nominally pure copper after undercoolings greater than 200° C. They showed that it could be produced however, in copper containing 0.08 wt % oxygen. Since copper, and copper-base alloys such as gun-metals and aluminium bronzes, are used extensively in the cast condition, the structure of highly undercooled copper ingots, and the mechanisms which produce structural refinement, are of great interest. The investigations described here were therefore undertaken to examine the following aspects of solidification in undercooled copper melts:

(i) The ease with which high purity copper can be undercooled by large amounts.

(ii) The structure of such highly undercooled ingots.

(iii) The mechanism causing spontaneous‡ recrystallisation.

(iv) The feasibility of producing it in high purity copper ingots by subsequent heat-treatment.

2. Experimental

100 to 150 g samples of 99.999% purity electrolytic copper were melted in silica crucibles and undercooled to various temperatures below

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‡"Spontaneous" is used here to mean "without prior deformation".

TABLE I Composition of Electrolytic Copper as Received (ppm)

Ag	Ni	Fe	Pb	As	S	O
5.4	0.5	0.3	0.2	0.2	4.0	6.0

the melting point before nucleation using the well-established soda-glass slag technique [6, 7]. Oxidation of the copper during immersion in the glass was minimised by using a flowing argon atmosphere in the furnace. An analysis of the copper as supplied is given in table I. Slight oxygen pick-up did occur during immersion of the copper in the glass, the amount depending on the expediency with which this was accomplished. An oxygen determination was performed on each specimen after test: these results are given in table II, together with the final amount of undercooling obtained in each of the ingots discussed here. Once a specimen was isolated from the atmosphere by the glass slag, the final oxygen content did not increase, even after long periods at high temperature.

TABLE II Undercooling and Oxygen Content of the Ingots Examined

Ingot no.	1	2	3	5	10	12
Undercooling, °C	103	135	163	64	78	193
Oxygen content, ppm	15	6	11	9	20	11
Ingot no.	13	15*	21*	22*	23*	24*
Undercooling, °C	206	188	194	207	182	183
Oxygen content, ppm	7	13	30	6	17	7

*Ingots quenched immediately after the completion of freezing.

After solidification the majority of the ingots were allowed to cool to room temperature in the furnace. Several were water-quenched immediately after completion of solidification to eliminate the effects on the structure of recovery during cooling. These ingots are indicated in table II.

The ingots were sectioned approximately through the point of nucleation (when it could be located from external examination) and prepared for metallographic examination. Macro-etching was carried out in acid ferric chloride solution and substructural features were revealed by a solution of 40 ml NH_4OH, 10 ml H_2O_2 and 50 ml water, which etched both the major grain boundaries and the substructure of dendrite elements within the grains. The mean dendrite element size was measured optically using a "Quantimet" image-analysing computer.

Heat-treatment of sectioned quenched ingots was carried out *in vacuo*. Annealing stages were carried out at 1000° C and the ingots could be charged into the hot zone while the furnace was at temperature.

X-ray crystallographic examination was performed by the back-reflection Laue technique using unfiltered Mo radiation, an accelerating voltage of 20 kV and a collimated beam of approximately 0.9 mm diameter.

3. Results

3.1. Undercooling

No difficulty was encountered in undercooling specimens by large amounts (> 200° C). In one instance an undercooling of 222° C was achieved but the specimen was not retained for examination and this high undercooling could not be repeated. Fig. 1 shows the progressive undercoolings obtained in a typical sample (ingot 12) which was finally allowed to cool in the furnace after nucleation at an undercooling of 193° C. It may be seen that, although there are occasional reversions, the general trend is that the undercooling increases with the number of cycles, or with time. The dashed lines in fig. 1 indicate

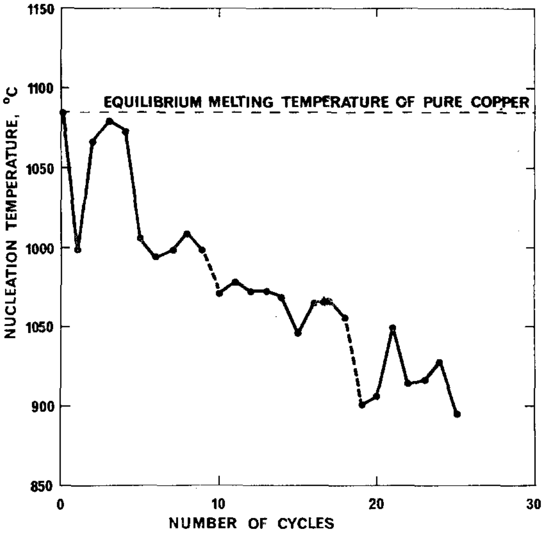


Figure 1 Progressive nucleation temperatures obtained for ingot 12. Final undercooling of 193° C was followed by furnace-cooling. Dashed lines indicated periods where the specimen was held above the melting temperature overnight.

periods during which the system was held above the melting temperature overnight. This was often followed, as shown, by a marked increase in the undercooling.

It occasionally proved difficult to undercool a melt past some point in the range 80 to 100° C, several consecutive cycles yielding the same undercooling. This could be overcome by superheating the melt to 1175° C and stirring it with the thermocouple sheath. This apparently either removed the offending nucleant or rendered it ineffective. On the other hand, once an undercooling of the order of 200° C was achieved, it could usually be repeated or improved upon as long as the melt was not disturbed and the superheat was kept to a minimum (< 1100° C).

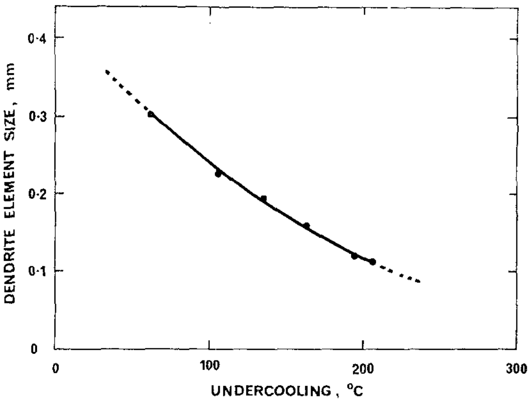


Figure 2 Relation between the final undercooling and the dendrite element size in the furnace-cooled ingots.

3.2. Structure

All the ingots in this investigation were undercooled more than 60° C, and appeared to nucleate at one point. As observed previously [7], the ingots constituted several grains which radiated out from the nucleation point and extended to the surface. No variation in the grain size with undercooling was observed and, in agreement with Powell and Hogan [7], no general recrystallisation was observed even at the highest undercooling. The crystallographic relationships between the simultaneously-nucleated grains in ingot 22 have been examined in detail [8]. It has been shown that the major grains are in twin orientation or bear some other simple crystallographic relationship to one another.

Within the grains, the size of the dendrite elements, as revealed by the etching, decreased progressively with increasing undercooling (fig. 2). The substructures within the grains of two typical ingots are delineated by the bold markings in fig. 3. These sub-grains, and those reported in fig. 2, are from furnace-cooled ingots and will therefore be larger, due to relaxation and recovery, than when formed during solidification. The more prominent substructure, which we identified with boundaries between neighbouring dendrite arms, enclosed a secondary substructure of less dense but well-aligned dislocation etch-pits (fig. 3a), which resembled those seen in metals annealed after cold-work. These were far better defined in ingots which had been furnace-cooled than in those quenched after solidification, indicating the effect of recovery processes. X-ray back-reflection patterns from the areas shown in

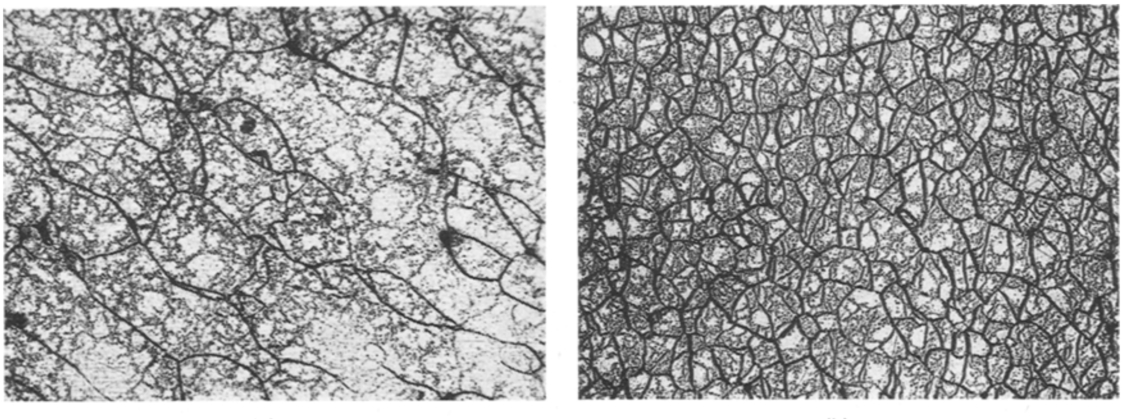

(a) (b)

Figure 3 Microstructures of two ingots showing the variation in the dendrite element size. (a) Ingot 2, $\Delta T = 135°$ C. (b) Ingot 12, $\Delta T = 193°$ C. Etched in NH_4OH/H_2O_2 (× 50).

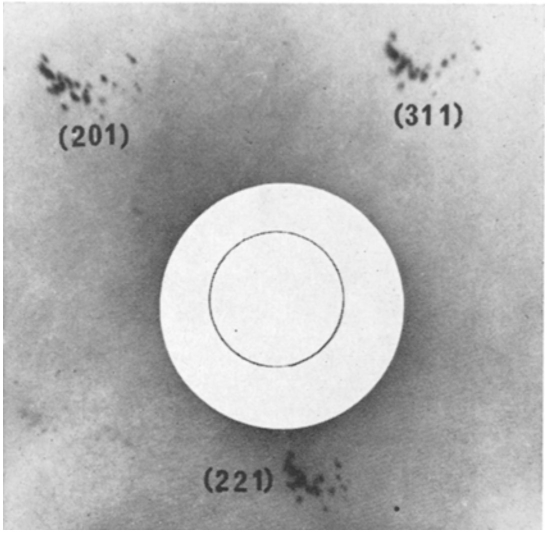


Figure 4 X-ray back-reflection (Laue) photograph taken from ingot 22 (area similar to that in fig. 3b), showing the sub-splitting of the diffracted beams (× 2).

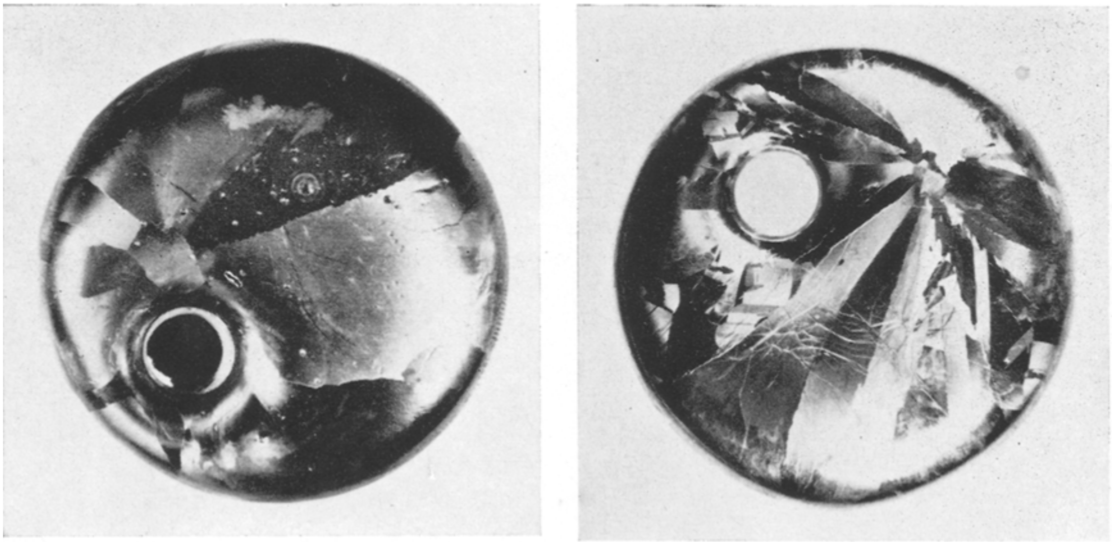
fig. 3 confirmed them to be single crystals containing marked substructure (fig. 4).

Ingots undercooled more than 190° C and then furnace-cooled were observed to contain numerous fine annealing twins indicating the onset of recrystallisation, although the major grain structure of the ingots was unchanged. No twins were observed in any of the quenched ingots. Fig. 5 shows two ingots undercooled by 163 and 193°C respectively, and furnace-cooled. It may be seen that the onset of twin formation is unmistakable. Increasing the undercooling from 190 to 206° C produced no discernible change in either the frequency of twin occurrence or the extent to which they advanced through the original grains.

Twin formation appeared in most cases to proceed by nucleation and growth from the original grain boundaries (fig. 6). Twins observed within the body of a grain, as for instance in fig. 6, most probably nucleated at boundaries outside the plane of the section. The etch-pitting technique indicated a far lower dislocation density within the new twin grains than in the original dendritic structure. The technique is however very sensitive to the orientation of the polished section [9] and cannot be relied on to confirm the absence of dislocations. However X-ray back-reflection photographs from the twins resulted in clean sharp spots, which indicated that no substructure was present. It was also established by this means that the composition plane of the twins was $\{111\}$-type as previously determined [8].

3.3. Annealing Experiments

Several of the ingots were annealed after cooling



(a) (b)

Figure 5 (a) Ingot 3, $\Delta T = 163^\circ$ C. (b) Ingot 12, $\Delta T = 193^\circ$ C. Showing the clear onset of twin formation in furnace-cooled ingots nucleated from melts undercooled by about 200° C. The approximate point of nucleation and the position of the thermocouples in the melt can also be seen. Etched in acid ferric chloride (× 1.5).

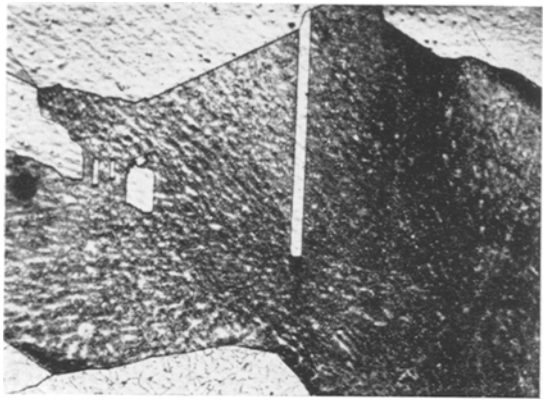
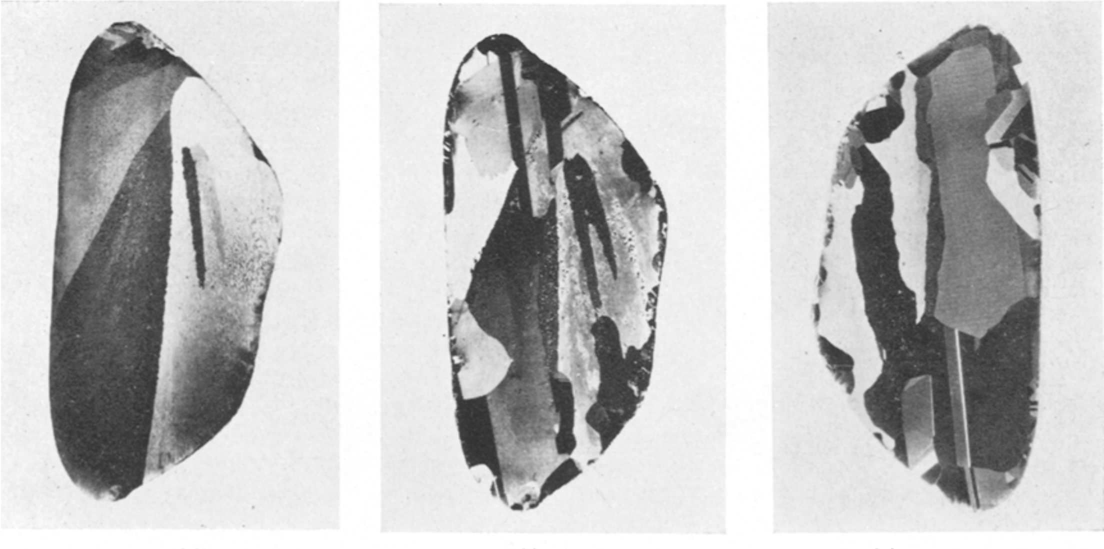


Figure 6 Section through ingot 13, $\Delta T = 206°$ C, showing the growth of twins into the original major grains during furnace-cooling. Nucleation occurred in the ingot below a point which may be seen in the lower right of the micrograph. The original grain boundaries in the section extrapolate back to this point. Etched in acid ferric chloride (× 5).

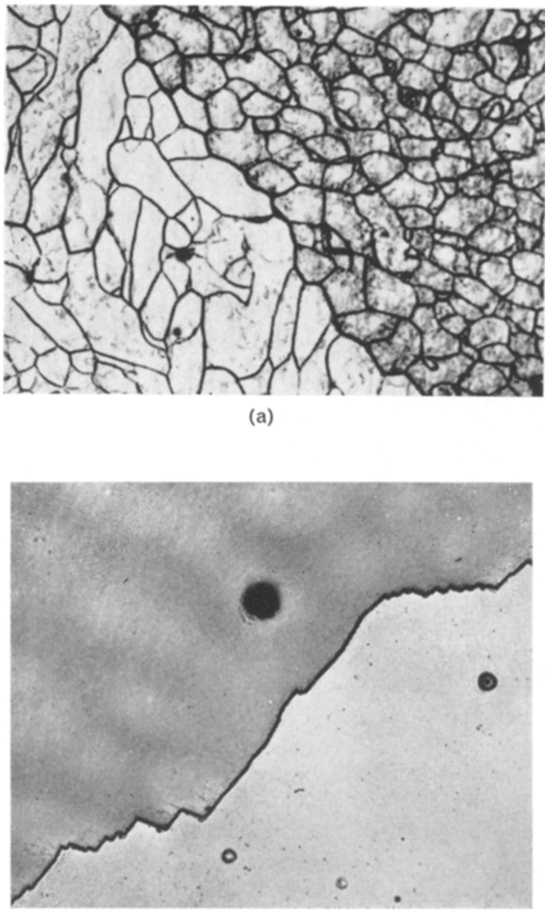
in order to check that annealing of ingots quenched after large undercoolings yielded twins of a similar nature to those observed in furnace-cooled ingots, to observe the manner in which these twins propagate into the originally-nucleated grains, and to examine the final structure of the ingots after complete annealing. Fig. 7 shows the effect of annealing on ingot 21, which undercooled 194° C before nucleation. Heating for only 10 min at 1000° C removes much of the radial grain structure present after solidification at high undercooling (fig. 7a), and is sufficient for twins to grow to a size visible at low magnification (fig. 7b). No general recrystallisation is observed however, even after annealing for 60 h at 1000° C as seen in fig. 7c. Although this long anneal removes the grown-in defect substructure, the final ingot remains substantially coarse-grained; the small grains on the periphery of the ingots (fig. 7c) are probably caused by the nucleation of new grains by surface damage during handling.

After quenching, the grain boundaries were irregular and appeared to follow the outlines of the sub-grain structure (fig. 8a); annealing for 10 min caused such boundaries to align themselves in a stepped fashion with $\{111\}$ twin planes in the adjacent grains [8]. Similar boundaries were found in the furnace-cooled ingots (fig. 8b). The onset of twinning involved the extension of these coherent twin boundaries into the neighbouring grain by motion of the connecting incoherent segments (fig. 9). In many cases the progressive motion of the grain boundaries during later annealing took place similarly by rapid migration of the incoherent segments in a stepped twin boundary. In other areas, annealing proceeded by migration of apparently random high-angle boundaries. However, these boundaries appeared to arise only after formation



(a) (b) (c)

Figure 7 Ingot 21 nucleated at an undercooling of 194° C. (a) Quenched on completion of freezing. (b) Annealed 10 min at 1000° C. (c) Annealed 60 h at 1000° C. Etched in acid ferric chloride (× 1.5).


(a)

(b)

Figure 8 Grain-boundary configurations in (a) ingot 15, $\Delta T = 188^\circ$ C, quenched on completion of freezing. Etched in NH_4OH/H_2O_2 (× 20). (b) Ingot 13, $\Delta T = 206^\circ$ C, furnace-cooled. Etched in acid ferric chloride (× 100).

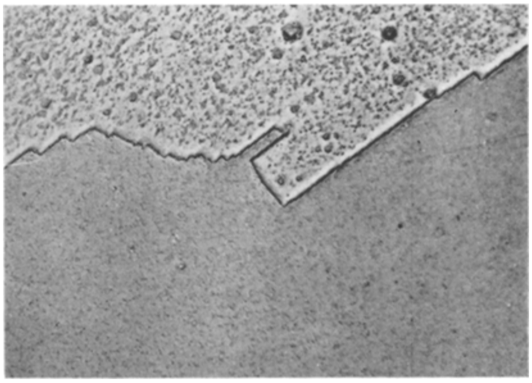


Figure 9 Propagation of boundaries during annealing by motion of noncoherent twin boundary segments. Ingot 22, $\Delta T = 207^\circ$ C, quenched on completion of freezing and subsequently annealed for 30 min at 1000° C. Etched in acid ferric chloride (× 250).

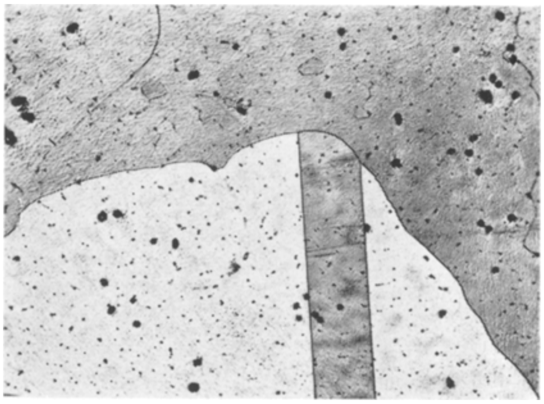


Figure 10 Random migrating boundary associated with twins: ingot 22, as fig. 9. Etched in acid ferric chloride (× 20).

initially of a twin boundary (fig. 10). Prolonged annealing moved such boundaries through the ingot, removing the original sub-grain structure, but as fig. 7c shows, it resulted in little or no diminution of the grain size.

4. Discussion

4.1. Nucleation of Undercooled Copper

Undercooling of pure copper, at least in small ingots, is very easy. It has been shown elsewhere [10] that undercoolings of about 50° C, when accompanied by the presence of oxygen, can cause grain refinement. In these investigations it has been shown that undercoolings of ~ 200° C may be obtained by repeated re-melting (fig. 1), or by prolonged heating of the melt above the melting point, in contact with a fluid glass slag. The mechanism by which the undercooling is increased seems likely to be the progressive removal of the more effective nucleants into the glass slag. However, the nature of these nucleants can only be guessed. It is unlikely that nucleation will be brought about by any of the possible impurities in the original copper (table I) since at the low concentrations at which they occur, these should be fully soluble even in the solid ingot and most certainly in the melt. It is considered more probable therefore that heterogeneous nucleation occurs on fine particles of refractory dust, introduced on the surface of the solid copper pieces during immersion. Powell has surveyed the available mechanisms for heterogeneous nucleation in silver [11], such as contact of the melt with devitrified (and hence crystalline) silica or glass, or with other ceramic crucibles, and also concluded that dust particles were likely to be the operating nucleants. We believe this to be the case in copper because nucleation was usually observed to occur within the body of the melt rather than at the surface. Nucleation by refractory particles also explains the occasional need to stir the melt to remove effective nucleants and the observation that once large undercoolings were obtained they could be repeated or improved, provided the melt remained uncontaminated. The few particles involved in the final nucleation must be relatively inefficient nucleants, since such large undercoolings were obtained in melts in contact with them. Powell has shown [11] that oxides in contact with molten silver are in fact inefficient nucleants, and by analogy we suggest that heterogeneous nucleation takes place in the present copper ingots on fine refractory oxide particles, introduced during immersion of the solid copper.

4.2. Recrystallisation after Undercooling

The reasons for the occurrence of recrystallisation in certain pure metal ingots solidified at high undercooling are not yet clear. Powell and Hogan [12] propose the driving force for such recrystallisation to be the large dislocation density grown into the material during high velocity growth. The intense additional grain-refinement found in Ag + 0.12 wt % O_2 they attribute to increases in the dislocation density due to the presence of dissolved oxygen during dendritic growth, and to deformation of the dendrites by evolution of this oxygen during the latter stages of freezing.

If this were the case with copper, however, one would expect a dislocation density sufficient to cause recrystallisation to be present in several ingots examined here. However, when these ingots are subsequently annealed to remove the grown-in defect substructure the grain configurations produced (fig. 7) do not resemble those found in highly undercooled silver.

It has already been demonstrated [10] that small amounts of oxygen (0.015 wt %) can produce a substantial grain-refinement in copper at low undercoolings, by dendrite fragmentation without recrystallisation. The close resemblance between the structures of copper and nickel ingots of similar oxygen content after equivalent amounts of undercooling [13] suggests that similar fragmentation processes take place in both materials. It seems likely therefore, that, in addition to a large undercooling prior to nucleation, dendrite fragmentation during growth is a prerequisite for general recrystallisation in low oxygen melts.

The effect of a fine as-cast grain size on the facility for recrystallisation in undercooled ingots is probably due to the enormous increase in the area of grain boundary within the ingot, which provides a much larger number of sites for nucleation of recrystallisation. Thus, when sufficient oxygen and undercooling are provided, recrystallisation will be relatively easy, even in ingots quenched shortly after solidification. In ingots with a very high impurity content, such as the copper + 0.08 wt % oxygen and silver +0.12 wt % oxygen alloys examined by Powell and Hogan [7, 12], the boundaries will be pinned by oxide particles and the original fine grain size retained. When far less oxygen is present, as in the nominally pure metals, considerable grain growth will ensue during and immediately after recrystallisation since the solid will be close to the melting point.

The dendrite arm re-melting process appears to require more than the 0.003 wt % oxygen contained in the present copper ingots. Experiments are presently in progress to obtain undercoolings of the order of 200° C in copper containing 0.015 wt % oxygen, and also in zone-refined samples of the recrystallising metals such as nickel and silver, in further attempts to clarify this question.

4.3. Grain-Boundary Migration

Figure 7 shows that annealing after solidification removes the as-cast grain structure, but produces no general grain refinement such as is observed in high-oxygen copper [7] and in other metals [4-6] after large undercoolings. The driving force for migration of the new grain-boundaries is the strain energy provided by the high density of structural defects in the original grains. The fine substructure within the grains immediately after solidification is evident in fig. 3, and its removal by annealing has been confirmed by X-ray examination.

Gleiter [14, 15] has shown that high-angle grain-boundaries have a stepped structure based on the $\{111\}$ crystal planes in fcc metals. Migration of a boundary occurs by the transfer of atoms from the steps of the shrinking grain to the steps of the growing grain, and the migration rate is related to the misorientation angle between the grains, and hence to the step density in the boundary [15]. It follows that coherent twin boundaries, being {111} planes in both crystals, contain no steps and therefore have a zero migration rate. Non-coherent twin boundaries on the other hand lie perpendicular to {111} planes and so have a maximum step density and a very high rate of migration [16].

We have previously shown [8] that a twin relationship may exist between adjacent crystals grown in a highly undercooled melt. Growth of one grain into its neighbour under these circumstances will produce twins, and since adjacent grains possess parallel {111}-type planes, the boundaries in furnace-cooled ingots often tend to align themselves in a gross step-like fashion along these planes, forming segments of coherent boundary and lowering the total energy of the system (fig. 8b).

The nucleation of small strain-free twins at such grain-boundaries can therefore readily occur and, once formed, the non-coherent twin boundary can migrate rapidly, removing the defect structure and forming long thin twins. Lateral growth of these twins can only proceed by migration of adjacent non-coherent segments in the same manner.

Since the twin orientation is uniquely defined by the relative orientations of the original grains, all the crystallisation nuclei on a given boundary will yield new twin grains of the same orientation. The coherent boundaries will therefore be eliminated eventually and one large strain-free grain will result. The final configuration of grains in the annealed ingot will depend on the progress of the non-coherent boundaries and their interaction with similar boundaries, and also with random migrating boundaries from other crystals.

5. Conclusions

In small high-purity copper melts undercooled before nucleation, the sub-grain size within the major grains decreases progressively as the undercooling is increased but, in agreement with an earlier report [7], no general recrystallisation occurs, by virtue of the high purity (or more precisely, the low oxygen content) of the melt. It seems likely that a necessary prerequisite for recrystallisation in undercooled copper is that a preliminary grain-refinement take place by some dendrite fragmentation process.

Annealing twins are found in high-purity ingots nucleated at undercoolings of more than 190° C and furnace-cooled; heat-treatment of quenched ingots produces similar twins. Prolonged annealing however, results in no significant reduction in grain size. The recrystallisation which occurs during the anneal proceeds mainly by migration of incoherent twin boundaries.

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Received 25 May and accepted 16 June 1970.