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NUCLEATION CATALYSIS IN COPPER ALLOYS

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PART II: UNDERCOOLING OF Cu-Al, Cu-Sn AND Cu-Zn ALLOYS

SUMMARY	i
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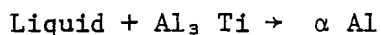
FIGURES 1 to 17

SUMMARY

The grain-size of small (≈ 50 g) samples of Cu-Fe alloys nucleated under controlled conditions of undercooling has been investigated. For hypoperitectic alloys, the grain structure varies markedly with the degree of undercooling. This variation is explained in terms of dendritic fragmentation. Using the technique of thermal analysis of bulk samples as a function of composition, it has been shown that γ Fe nucleates α Cu in Cu-Fe alloys of peritectic composition. Grain refinement in Cu-Fe alloys of peritectic composition occurs in part as the result of fragmentation of copper dendrites after nucleation of copper by iron.

1. INTRODUCTION

Investigations of the factors controlling the grain-size of cast metals and alloys have been actively pursued with relation to aluminium and its alloys¹⁻¹⁸. When titanium is added to aluminium and its alloys, the grain-size decreases markedly when the titanium composition is sufficiently high for the peritectic reaction

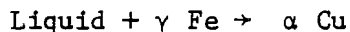


to occur.

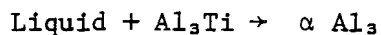
The following hypotheses have been proposed to account for this change:

1. Nucleation of aluminium by intermetallic compounds^{3,8,9,11,12,13,16,18}.
2. Restriction of crystal growth by concentration gradients, as suggested by Northcott^{19,20}, in conjunction with nucleation of aluminium by intermetallic compounds². The bulk of investigational work has been directed towards identification of the intermetallic compounds responsible for nucleation of the Al_3Ti or aluminium.

Copper and copper-based alloys are traditionally refined by adding sufficient iron for the peritectic reaction



to occur²¹⁻²⁴. Iwase *et al.*²³ consider the grain-refining effects of pro-peritectic iron to be the results of fragmentation of primary iron crystals during the peritectic reaction. The hypothesis that the primary pro-peritectic phase is fragmented by the peritectic reaction has been applied to other systems, but disputed for the reaction



by Crossley and Mondolfo³ and Delamore and Smith¹³.

Using an entirely different experimental method, Tarshis *et al.*²⁵ have shown that grain refinement can occur in alloys in which heterogeneous nucleants are not present. These workers have shown that, for aluminium alloys,

the grain size of castings is small when the parameter

$$\frac{m_L(1-k_0)C_0}{k_0}$$

is large, where m_L is the liquidus slope,

k_0 is the solute distribution coefficient, and

C_0 is the nominal solute concentration.

This part of the annual report describes the results of experiments carried out to investigate the nature of the grain-refining mechanism of iron in copper, using alloys capable of undercooling in a manner similar to that of Tarshis *et al.* coupled with a technique for the study of nucleation in peritectic systems previously described by the author³⁶.

2. REVIEW OF UNDERCOOLING TECHNIQUE FOR EVALUATION OF NUCLEATION CATALYSIS IN PERITECTIC SYSTEMS

The experimental method applied to the investigation of nucleation behaviour in peritectic systems is explained with reference to Figure 1. A 50-g sample of composition X (hypoperitectic composition) is consistently undercooled $\geq 100^\circ\text{C}$. A typical cooling curve is shown as curve A in Figure 2. Additional B is added to change the composition of the alloy to a higher hypoperitectic composition represented by Y, Figure 1. The typical cooling curve for composition Y is as for composition X, i.e. curve A, Figure 2. More B is added to change the composition of the alloy to the peritectic composition, represented by composition Z in Figure 1. The cooling curve recorded consistently for this composition is shown as curve B in Figure 2. When sufficient A was added to return the sample composition to alloy Y, the original cooling curve represented by curve A in Figure 2 was obtained.

The cooling curves in Figure 2 have been explained in the following terms. In an alloy of composition Y, curve A in Figure 2, the melt undercooled until the α solid solution was nucleated at point a. Rapid dendritic growth of the α phase recalesced the temperature to point b. For the sample of composition Z, curve B in Figure 2, nucleation of primary β occurred at point c followed by slight recalescence to point d. Growth of the primary β continued

as the temperature fell from point d to the peritectic temperature. Nucleation of the α phase took place at point e, say 1°C below the peritectic temperature. The variation in the undercooling of the α as a function of composition of the alloy can be interpreted in terms of the nucleating ability of the β for α . When the alloy composition is changed from Y to Z, the undercooling for nucleation of the α phase decreased from $\geq 100^\circ\text{C}$ to $\approx 1^\circ\text{C}$. This suggests that the primary β nucleates α at $\approx 1^\circ\text{C}$ below the peritectic temperature. When sufficient A was added to return the alloy composition to Y, the undercooling for nucleation of α increased to the original range, $\geq 100^\circ\text{C}$ below the α liquidus. This supports the suggestion that β is an efficient nucleant for α since any other nucleant inadvertently added with the B in the peritectic alloy would also be expected to reduce the undercooling in the subsequent hypoperitectic case.

It might be argued that these data may also be interpreted in terms of changes of the nucleation characteristics of the α phase - e.g., change in lattice spacing - for the different α and liquid phase compositions in the hypoperitectic and peritectic cases. The results of a large number of experiments using bulk samples of undercooled alloys^{25,27,28,29,30} of different solute and solvent species have shown that if, e.g., a Cu - 1 wt % Zn alloy will undercool $\geq 100^\circ\text{C}$, a Cu - 30 wt % Zn alloy will also undercool $\geq 100^\circ\text{C}$. These results support the hypothesis that a heterogeneous nucleant ineffective in an alloy of 1 wt % alloying element is also ineffective in an alloy of 30 wt % alloying element and vice versa. Though the nucleation characteristics of the α phase for the different α and liquid phase compositions may change, the efficiency of the heterogeneous nucleants remaining in the undercooled sample does not change over large variations of solute concentration, commonly 30 wt %. If, in peritectic systems, heterogeneous nucleants are ineffective at undercoolings $< 100^\circ\text{C}$ in alloys from 1 wt % solute to a composition within 1 wt % of the start of the peritectic reaction, it is reasonable to assume that the heterogeneous nucleants will not be effective at the peritectic composition. The technique of monitoring undercooling as a function of composition would appear to be an acceptable method of studying nucleation phenomena, provided that it was shown that there was no change in the efficiency of the remaining heterogeneous nucleants as a function of composition. For peritectic systems, the efficiency of the remaining heterogeneous nucleants as measured by undercooling should not change within the

composition range 1 wt % solute to a solute concentration slightly less than that at which the peritectic reaction occurs.

3. EXPERIMENTAL PROCEDURE

The experimental procedure was similar to that used previously by the author³¹. The copper was nominal 99.9% purity, oxygen-free, high-conductivity copper, the major impurities of which were iron, zinc and silicon. Two grades of iron were used: Specpure Iron from Johnson-Matthey Chemicals Ltd, England, of 5/8 purity, and commercial mild-steel welding wire of approximately 0.2 wt % C content. Melting was carried out in open-ended vertical cylindrical furnaces wound with Kanthal Al wire.

The undercooling technique previously used for copper and copper alloys was employed^{27,31}. Samples of copper weighing 50 g were prepared by adding 10-g pieces of copper to a vitreous silica crucible partly filled with commercial soda-lime glass at a temperature of approximately 1000°C. Each piece was quickly immersed in the glass slag and held at this temperature until any oxide coating on the surface decomposed. This change was easily observed, and coincided with the formation of gas bubbles in the glass at the sample-glass interface. The temperature of the furnace was raised to melt the copper, then lowered to approximately 1000°C, and another piece of copper was added. By following this procedure for all pieces, the oxygen content was kept to a minimum. After 50 g of copper had been melted, a similar procedure was adopted for the addition of iron to the melt. A Pt/Pt - 13% Rh thermocouple enclosed in a vitreous silica sheath was immersed in the melt for temperature measurement. The Pt/Pt - 13% Rh thermocouples were calibrated *in situ* against the melting point of pure copper. Temperatures were recorded on a variable-scale potentiometric chart recorder with zero suppression. By varying the millivoltage scale of the recorder, it was possible to measure the temperature with a precision of $\pm 1^\circ\text{C}$.

3.1 Grain-Size v. Undercooling Experiments for Hypoperitectic Alloys

The melt was held at 50 - 100°C superheat before the first cooling curve was taken by reducing the power to the furnace. After a cooling curve was recorded, the sample was reheated to 50 - 100°C superheat and held at this temperature for 24 h before the next cooling curve was taken. This procedure was repeated several times to determine the undercooling at which the partic-

ular alloy composition would undercool spontaneously and consistently. Initially, the sample was held in the furnace until solidification was complete, after which it was quenched in water. Later, experiments similar to those reported by Tarshis *et al.*²⁵ were conducted using a technique described previously by the author³². After a consistent undercooling ($\geq 100^\circ\text{C}$) was obtained, the sample was remelted, held at 50 - 100°C superheat for 24 h and undercooled to 75°C below the liquidus, at which point the power to the furnace was adjusted to increase the temperature of the molten sample to the desired nucleation temperature. Nucleation was effected by pushing copper wire through the overlying glass slag to nucleate the melt at the top surface. Immediately after nucleation, the power to the furnace was switched off and the sample held in the furnace until nucleation was complete (approximately 20 min) after which it was quenched in water.

3.2 Nucleation Studies by the Thermal Analysis of Bulk Samples as a Function of Changing Composition

According to Hansen³³, the peritectic composition in the Cu-Fe system is Cu - 4.0 wt % Fe and the peritectic reaction isotherm extends from 2.8 wt % Fe to ≈ 91.5 wt % Fe. Initially, samples of Cu - 1 wt % Fe were undercooled $\geq 100^\circ\text{C}$. Additions of iron to change the composition progressively from 1 wt % Fe to 2 wt % Fe and then to 2.75 wt % Fe were made; thermal analysis showed that the undercooling was consistently $\geq 100^\circ\text{C}$, so that the undercooling was not affected by iron content within the range 1 - 2.75 wt % Fe. This indicates that the heterogeneous nucleants remaining in the sample are ineffective at undercoolings $< 100^\circ\text{C}$ within the composition range Cu - 1 wt % Fe to Cu - 2.75 wt % Fe. On this evidence, it was assumed that heterogeneous nucleants would not be effective at small degrees of undercooling (say 5 or 10°C) in an alloy of 2.8 wt % Fe - i.e., the composition of the liquid at the peritectic temperature.

On this basis, the following experimental procedure was adopted. Samples of Cu - 2 wt % Fe of hypoperitectic composition (V - Fig. 3) were consistently undercooled $\geq 100^\circ\text{C}$. Sufficient iron was added to change the composition of the alloy to the peritectic composition, represented by W in Figure 3. After consistent thermal analysis data were obtained for the peritectic composition, sufficient copper was added to return the sample to composition V in Figure 3 i.e., Cu - 2 wt % Fe. To elucidate the transformations occurring during the cooling of samples of peritectic composition, samples were quenched from

various points on the cooling curve prior to, and following, nucleation of the copper in the presence of peritectic iron.

The glass slag was removed from the samples by dissolution in cold hydrofluoric acid and sectioned vertically for metallographic examination. Selected samples were analysed for iron content to check the composition of the samples.

4. RESULTS

4.1 Grain-Size as a Function of Undercooling for Hypoperitectic Alloys

The characteristic features of the microstructure of the many samples of Cu - 2 wt % Fe produced are illustrated in Figures 4-10 inclusive. When a sample had nucleated as close as practicable to the melting point ($\leq 1^\circ\text{C}$ undercooling), a coarse-grained microstructure was obtained - Figure 4. Figure 5 illustrates the double grain structure of samples nucleated at 2°C undercooling. The top central region consists of fine grains while the remainder is coarse-grained. The grain structure of the sample nucleated at 29°C undercooling is illustrated in Figure 6. Reasonably large grains showing dendritic segregation cover the top of the sample, beneath which the sample is fine-grained. These features, although varying in detail, were characteristic of all samples nucleated at undercoolings between 3°C and 50°C . For samples nucleated at undercoolings between 50°C and 70°C , the grain structure of a sample nucleated at 66°C and shown in Figure 7 is representative. The sample of Figure 7 has a duplex grain structure - small equi-axed crystals within large grains. The detail of the duplex grain structure is shown in Figure 8 and 9 where small equi-axed grains are shown within a segregation pattern. Using the etch-pit technique described previously by the author^{27,31,32}, it was determined that the equi-axed grain structure within the large grains was not a low-angle substructure but that the boundaries between the small grains and the large grains were of a high angle. When the undercooling at which a sample was nucleated exceeded 70°C , a coarse grain-size was obtained - Figure 10. Similar results were obtained for Cu - 1 wt % Fe and Cu - 2.75 wt % Fe. No detectable difference was found between the Specpure Iron of 99.99% purity and commercially pure 0.2 wt % C steel.

4.2 Nucleation Studies by the Thermal Analysis of Bulk Samples as a Function of Changing Composition

Samples of Cu - 2 wt % Fe (hypoperitectic composition) were consistently

undercooled $\geq 100^{\circ}\text{C}$ before sufficient iron was added to change the composition to Cu - 4 wt % Fe (the peritectic composition). The cooling curves obtained were similar to those illustrated in Figure 2. The Cu - 2 wt % Fe sample undercooled $\geq 100^{\circ}\text{C}$ as for curve A while the cooling curve for the Cu - 4 wt % Fe sample was similar to curve B. Following curve B, iron was nucleated at temperature c and copper was nucleated in the presence of primary iron at temperature e, 1°C below the peritectic temperature. When sufficient copper was added to the melt to return the composition to the hypoperitectic composition of Cu - 2 wt % Fe, the original undercooling of $\geq 100^{\circ}\text{C}$ was obtained.

The fine-grain structure of a Cu - 4 wt % Fe alloy (peritectic composition), quenched after the cooling curve indicated that solidification was complete, is presented in Figure 11. Detail of the shell-like nature of the primary iron is given in Figure 12. The primary iron tended to be uniformly distributed throughout the sample. Figure 13 is a typical cooling curve for the alloy of peritectic composition and shows the temperature C at which the sample of Figure 11 was quenched in water. When samples were quenched from a temperature A above the peritectic temperature, a mixed grain structure represented by that of Figure 14 was obtained. Finer grains were concentrated towards the middle of the sample and extended from top to bottom. The finer grains were usually associated with dendrites of iron - Figure 15. The cooling curve invariably displayed a small plateau just below the peritectic temperature. When samples were quenched from the plateau, a variable fine-grain structure was obtained - Figure 16. In this sample, the iron existed as dendrites at the top surface - Figure 17.

5. DISCUSSION

5.1 Grain-Size as a Function of Undercooling for Hypoperitectic Alloys

With the exception of the results for nucleation at 1°C and 2°C undercooling, the results for samples of alloy compositions Cu - 1 wt % Fe, Cu - 2 wt % Fe and Cu - 2.75 wt % Fe, are in good agreement with those of Tarshis *et al.*²⁵ for Ni - 5 wt % Cu, Ni - 10 wt % Cu, Ni - 20 wt % Cu, and Ni - 30 wt % Cu composition. Tarshis *et al.* imply that the small grain-size (within the range 3°C to 50°C undercooling for Cu - Fe) and the duplex grain structure (within the range 50°C to 70°C for Cu - Fe) result from a dendrite fragmentation mechanism²⁴. Similarly, a fine grain-size in samples of undercooled Cu - 0.02 wt % O and Cu -

2.5 wt % Sn alloys undercooled $\leq 60^{\circ}\text{C}$ has been attributed to dendrite fragmentation^{35,36}. Following Tarshis et al., theories requiring nucleation cannot explain the fine-grain structure of samples nucleated at undercoolings within the range 3°C to 50°C undercoolings (Fig. 6), since the required heterogeneous nucleants are not present in the melt. Although samples were quenched when the cooling curve indicated that solidification was complete, some grain-growth may have occurred. However, it is felt that the grain structure as shown in Figures 4-10 is a close approximation to that existing in the samples at the completion of solidification. It seems reasonable to conclude that the following mechanism produced the grain structure of Figure 6 (representative of nucleation in the undercooling range $3^{\circ}\text{C} - 50^{\circ}\text{C}$). The copper-wire probe nucleated several grains from which dendrite fragments were detached, producing the fine equi-axed grain size. As the undercooling at which nucleation is induced is increased, the proportion of the melt frozen by dendritic growth during recalescence is increased. The duplex grain structure of Figures 7, 8 and 9 probably results from fragmentation of dendrites under conditions where a dendrite fragment cannot move freely through the melt, and hence is confined to the region from which it was detached, producing fine grains within the original large grains. With further undercooling, dendritic growth is more complete and no fragmentation occurs - Figure 10 (representative of samples nucleated at undercoolings in the range $70^{\circ}\text{C} - 100^{\circ}\text{C}$). An occasional straight-line boundary indicative of a twin relationship across the boundary was observed, but the high incidence of annealing twins previously observed in undercooled alloys containing oxygen^{27,31,32} did not occur. The incidence of straight-line boundaries was related to the oxygen content which in these Cu - Fe alloys was purposely kept low (verified by metallography).

Tarshis et al. report an increase in grain-size as the undercooling is decreased towards 0°C undercooling for Ni - 5 wt % Cu and Ni - 10 wt % Cu, although the variation is not nearly as great as that reported here for Cu - 2% Fe alloys. According to Tiller and O'Hara³⁷, dendrites growing into an undercooled melt contain more than the equilibrium solute concentration, since they form at temperatures between the melt and recalescence temperatures. Fragmentation of dendrites occurs as the result of the high solute dendrites decomposing as the temperature is increased by the release of latent heat. A sample nucleated as close as practicable to the liquidus temperature would not be expected to undergo dendrite fragmentation (Fig. 4) since the solute content of the dendrites would approach the equilibrium solute concentration

Surprisingly to the author, the grain structure changed markedly over a narrow range of undercooling at low undercooling values. At undercoolings $\leq 1^\circ\text{C}$, the samples were coarse-grained (Fig. 4) while at undercoolings from 3°C to 50°C the samples were fine-grained with a few coarser grains at the top surface - Figure 6. At an intermediate undercooling of 2°C , the grain structure as illustrated in Figure 5, showed a coarse grain-size similar to the sample of undercooling of $\leq 1^\circ\text{C}$ with the addition of a top central region of fine equi-axed grains. The fine equi-axed region probably forms by dendrite fragmentation towards the end of solidification as the thermal gradient decays and the temperature in this region increases sufficiently for fragmentation to occur.

5.2 Nucleation Studies by the Thermal Analysis of Bulk Samples as a Function of Changing Composition

Since a sample of hypoperitectic composition (Cu - 2 wt % Fe) undercooled $> 100^\circ\text{C}$ after the composition has been changed to the peritectic composition (Cu - 4 wt % Fe) and then back to the hypoperitectic composition, it is suggested that no heterogeneous nucleant was inadvertently added with the iron in the peritectic alloy because the added heterogeneous nucleant would be expected to reduce the undercooling in the subsequent hypoperitectic case. The question that must be answered at this point is whether the primary γ iron nucleated the α copper at temperature e (Fig. 2) or whether the nucleation characteristics of the α copper are different in the melt of slightly higher iron content. As suggested previously, it is considered that iron is the nucleant for copper as it has been shown that the efficiency of the heterogeneous nucleants remaining in the sample does not change over the solute range 1 - 2.75 wt % Fe, and it seems reasonable to assume that the efficiency of the heterogeneous nucleants will not change over the range 1 - 2.8 wt % Fe where 2.8 wt % Fe is the composition of the liquid in equilibrium with primary iron at the peritectic temperature. Further proof that iron nucleates copper at e will be presented in the following discussion.

5.3 The Mechanism of Grain Refinement in Peritectic Cu-Fe Alloys

Previous studies of the effect of additions of iron to copper and copper-based alloys^{23,38} has shown that no grain refinement occurred until sufficient iron was added for the peritectic reaction to occur. The results reported here confirm that conclusion. When samples of hypoperitectic composition were

nucleated at $\leq 1^\circ\text{C}$ undercooling, a large grain-size was obtained (Fig. 4) whereas a much finer grain-size was obtained when a sample of peritectic composition was solidified and the cooling curve showed that primary iron nucleated copper at 1°C undercooling below the peritectic temperature - Figure 11. According to Iwase *et al.*²³, refinement by the addition of iron occurs as a result of the peritectic reaction disintegrating the iron dendrites such that the iron fragments behave as separate nuclei for further peritectic reaction. As a result of this early work by Iwase *et al.* many peritectic systems were investigated in both the aluminium and copper systems to determine whether the peritectic reaction, *per se*, would produce grain refinement. This was investigated, e.g., for three peritectic systems Al - Ti, Al - Zr and Al - Cr, by Delamore and Smith¹⁵ who found that the results for Al - Zr and Al - Cr differed from that for Al - Ti and indicated that the peritectic reaction itself was not sufficient for grain refinement.

The following explanation is proposed for the fine grain-size of the sample of peritectic composition described in this Report. In the prior discussion of nucleation as a function of changing composition, it was concluded that iron nucleated copper in alloys of peritectic composition. This conclusion is supported by metallographic evidence shown in Figure 15, which suggests that the small copper grains surrounding the iron dendrites have been nucleated by the iron dendrites. Proceeding now to Figures 16 and 17 which illustrate the grain structure of samples of peritectic composition quenched after copper was nucleated by iron, it will be seen that the sample is fine-grained throughout (Fig. 16) although iron dendrites exist only at the top surface (Fig. 17) and therefore could not have nucleated the fine grains at the bottom of the sample. It is proposed that the fine grains at the bottom result from fragmentation of copper dendrites nucleated by the iron dendrites at the top of the sample. This suggestion is supported by the results of the grain size of undercooled samples of hypoperitectic composition (Cu - 2 wt % Fe) discussed in the previous section. It was suggested that dendrite fragmentation occurred at undercoolings as small as 2°C below the liquidus. This would suggest that dendrite fragmentation would occur at undercoolings of the same order, or even smaller, in melts of peritectic composition, since these melts would contain more solute and hence would be more likely to fragment according to the parameter,

$$\frac{m_L(1-k_0)C_0}{k_0}$$

of Tarshis *et al.*²⁵. After fragmentation of the copper dendrites, it is to be expected that natural convection would stir the melt³⁹ distributing the iron dendrites through the sample. It might be asked why the iron dendrites of Figure 14 were not confined to the top of the sample instead of being positioned in the central region. The probable explanation for this was that, in lifting the crucible containing the metal and thermocouple-sheath out of the furnace prior to quenching in water, it was not possible to prevent agitation of the melt by the thermocouple-sheath.

Although the explanation for the grain size of the samples of peritectic composition seems reasonable, the author is reluctant to offer this explanation for the grain refinement role of iron in commercial casting practice without a word of caution. The results reported here may be a function of the experimental conditions. The author is reminded of the work of Cole and Bolling⁴⁰ who showed that the various theories of the columnar-to-equiaxed transition in ingots could be substantiated by performing the appropriate experiments. Nevertheless, in agreement with Tarshis *et al.*, it appears that a fine grain-size in castings may be the result of dendrite fragmentation as well as an increased rate of nucleation by the addition of heterogeneous catalysts.

6. CONCLUSIONS

1. When samples of Cu - 2 wt % Fe alloy (hypoperitectic composition) are nucleated at various degrees of undercooling between 1°C and 100°C undercooling, the grain structure obtained is dependent on the range of undercooling at which nucleation was induced by a copper wire.
 - a. Undercooling \leq 1°C, coarse grain structure
 - b. Undercooling 1°C - 3°C, double grain structure
 - c. Undercooling 3°C - 50°C, fine grain structure
 - d. Undercooling 50°C - 70°C, duplex grain structure
 - e. Undercooling 70°C - 100°C, coarse grain structure

These variations are explained in terms of dendritic fragmentation and are substantially in agreement with the results of Tarshis *et al.*²⁵ for Ni - 5 wt % Cu, Ni - 10 wt % Cu, Ni - 20 wt % Cu, and Ni - 30 wt % Cu alloys.

2. Using the technique of thermal analysis of bulk samples as a function of composition described previously for the peritectic system by the author²⁶, it has been shown that γ Fe nucleates α Cu in Cu-Fe alloys of peritectic composition.
3. Grain refinement in Cu-Fe alloys of peritectic composition occurs in part as the result of fragmentation of copper dendrites after nucleation of copper by iron.

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PART II: UNDERCOOLING OF Cu-Al, Cu-Sn AND Cu-Zn ALLOYS

SUMMARY

In order to investigate the mechanism of grain refinement by the addition of alloying elements such as titanium, boron, etc. to copper-based alloys, it is necessary to produce undercooling in the various copper-based alloys of commercial significance. To this end, experimental procedures have been developed to produce undercooling $\geq 100^{\circ}\text{C}$ in Cu-Al, Cu-Sn, and Cu-Zn alloys. Master alloys of Cu-B and Cu-Ti have been undercooled $\geq 40^{\circ}\text{C}$. This part of the project has just started and the experimental programme is being planned based on the results for the Cu-Fe alloys.

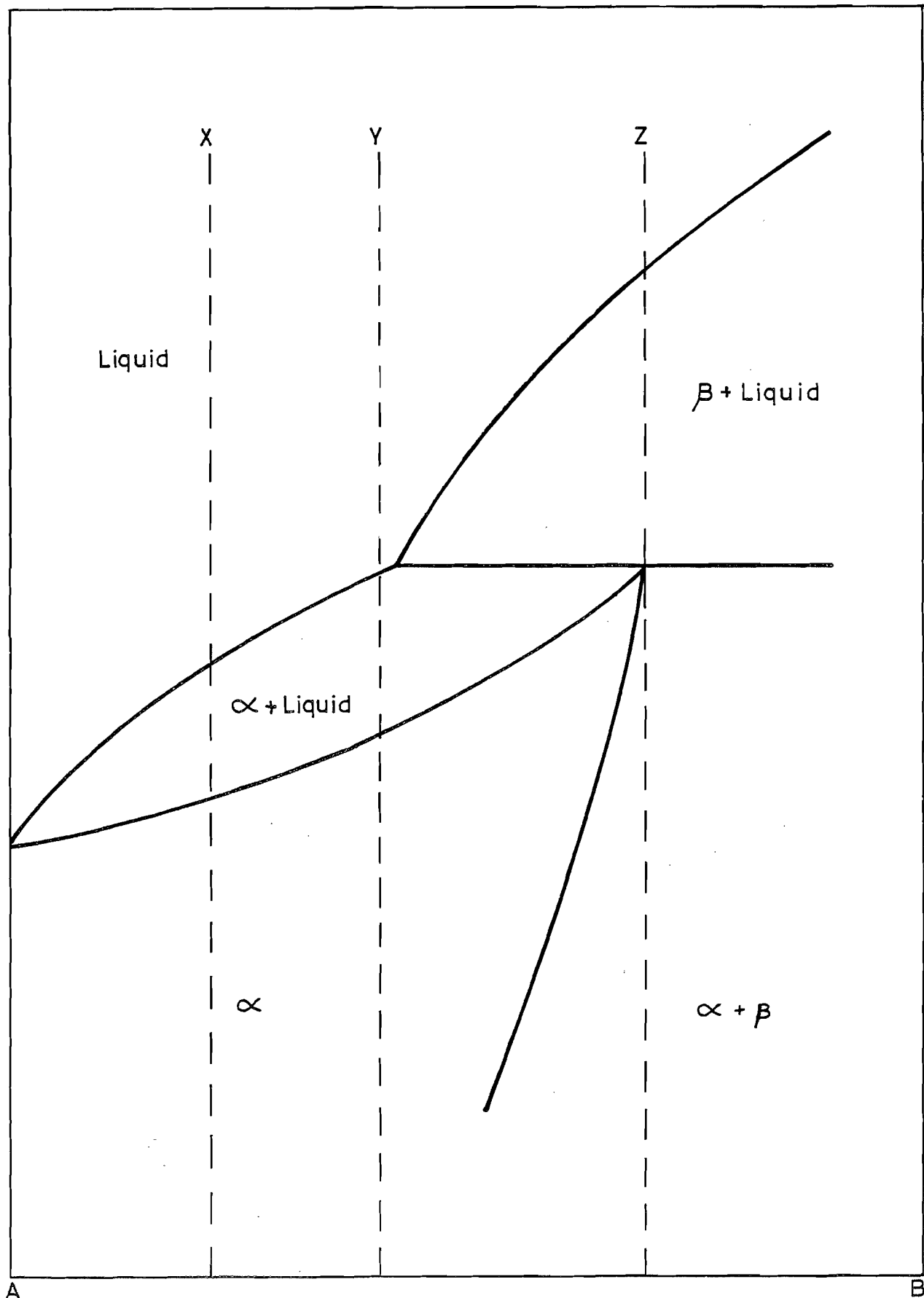


Fig.1: PART OF BINARY PERITECTIC SYTEM USED FOR NUCLEATION STUDIES. X&Y ARE HYPOPERITETIC COMPOSITIONS WHILE Z IS THE PERITECTIC COMPOSITION

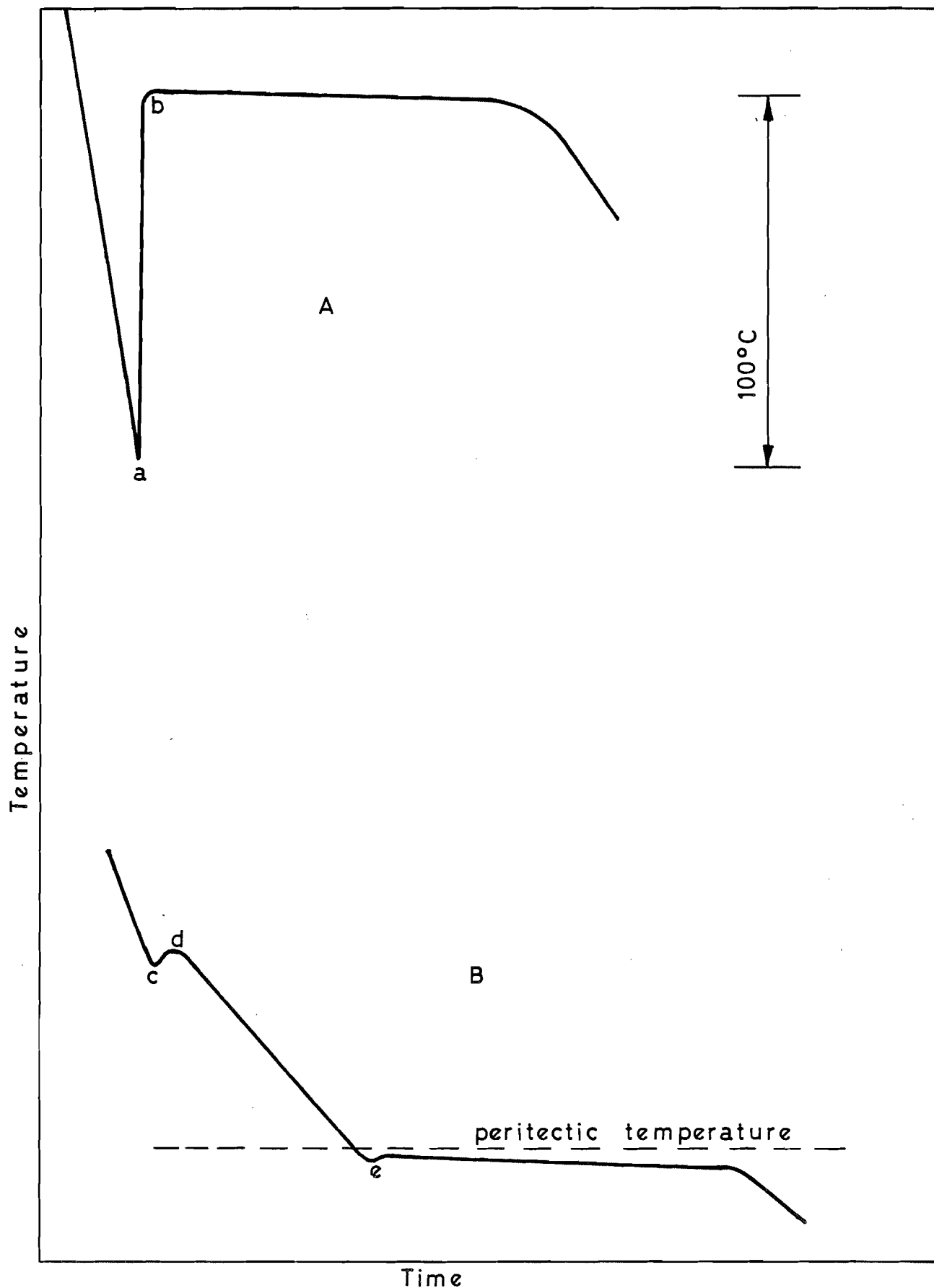


Fig.2: CURVE A - COOLING CURVE FOR HYPOPERITECTIC COMPOSITIONS (X&Y in Fig.1). CURVE B - COOLING CURVE FOR PERITECTIC COMPOSITION (Z in Fig.1)

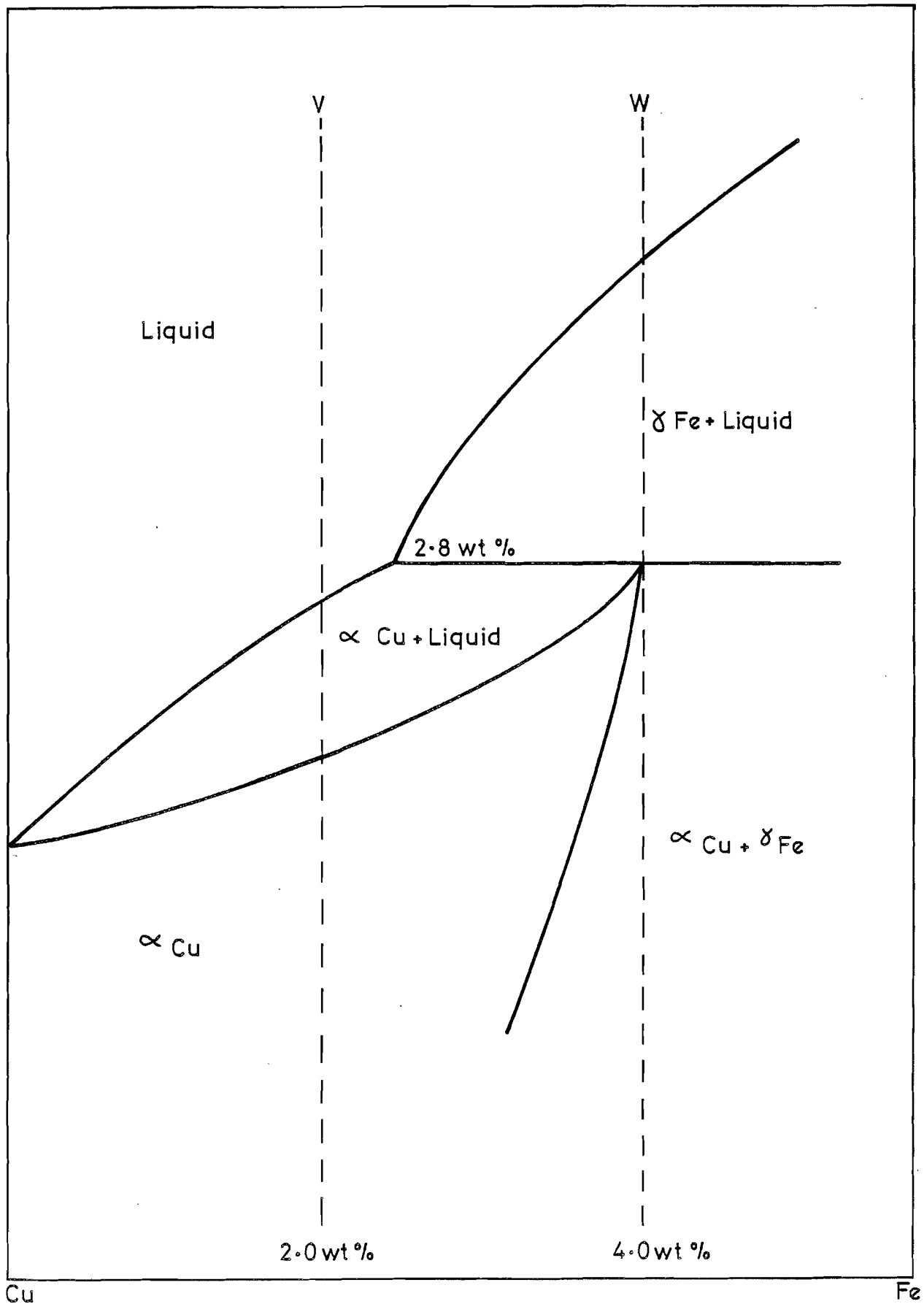


Fig.3: PART OF THE Cu-Fe PHASE DIAGRAM IN THE REGION OF THE PERITECTIC REACTION $\text{LIQUID} + \delta \text{Fe} \rightarrow \alpha \text{Cu}$. THE COMPOSITION OF THE ALLOYS ARE V (HYPOPERITECTIC, 2wt% Fe) AND W (PERITECTIC, 4wt% Fe)



FIG. 4

Mag. 5x

PHOTOMICROGRAPH OF HALF VERTICAL SECTION SHOWING COARSE GRAIN STRUCTURE OF SAMPLES OF Cu - 2 WT % Fe NUCLEATED BY COPPER WIRE AT $\leq 1^{\circ}\text{C}$ UNDERCOOLING. THE DARK INTERDENDRITIC REGION IN THE BOTTOM LEFT-HAND CORNER IS POROSITY.



Mag. 5x

FIG. 5

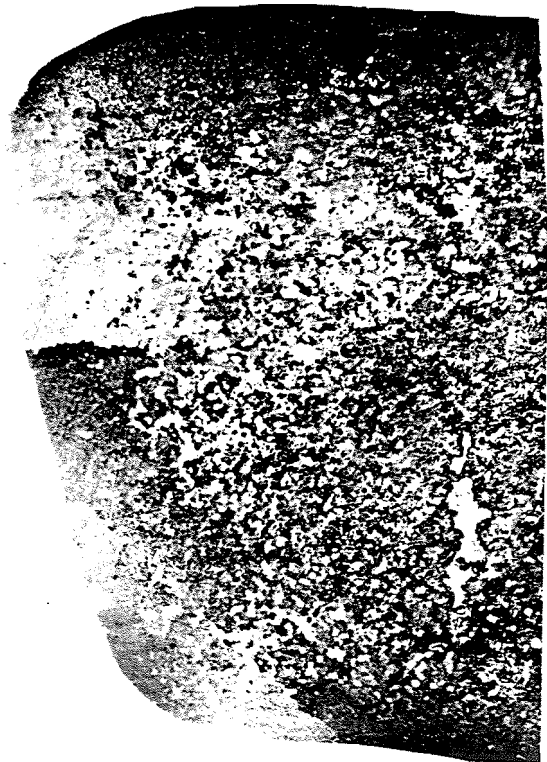
PHOTOMICROGRAPH OF HALF VERTICAL SECTION SHOWING DOUBLE GRAIN STRUCTURE OF SAMPLES OF Cu - 2 WT % Fe NUCLEATED BY COPPER WIRE AT 2°C UNDERCOOLING. THE TOP CENTRAL REGION IS FINE-GRAINED WHILE THE REMAINDER IS COARSE-GRAINED.



FIG. 6

Mag. 5x

PHOTOMICROGRAPH OF HALF VERTICAL SECTION SHOWING GRAIN STRUCTURE OF SAMPLE OF Cu - 2 WT % Fe NUCLEATED BY COPPER WIRE AT 29°C UNDERCOOLING. REASONABLY LARGE GRAINS SHOWING DENDRITIC SEGREGATION COVER THE TOP OF THE SAMPLE BENEATH WHICH THE SAMPLE IS FINE-GRAINED, REPRESENTATIVE OF SAMPLES NUCLEATED BETWEEN 3°C AND 50°C UNDERCOOLING.



Mag. 5x

FIG. 7

PHOTOMICROGRAPH OF HALF VERTICAL SECTION SHOWING DUPLEX GRAIN STRUCTURE OF SAMPLE NUCLEATED AT 66°C UNDERCOOLING. SMALL EQUI-AXED GRAINS WITHIN LARGE GRAINS, REPRESENTATIVE OF SAMPLES NUCLEATED BETWEEN 50°C AND 70°C UNDERCOOLING.

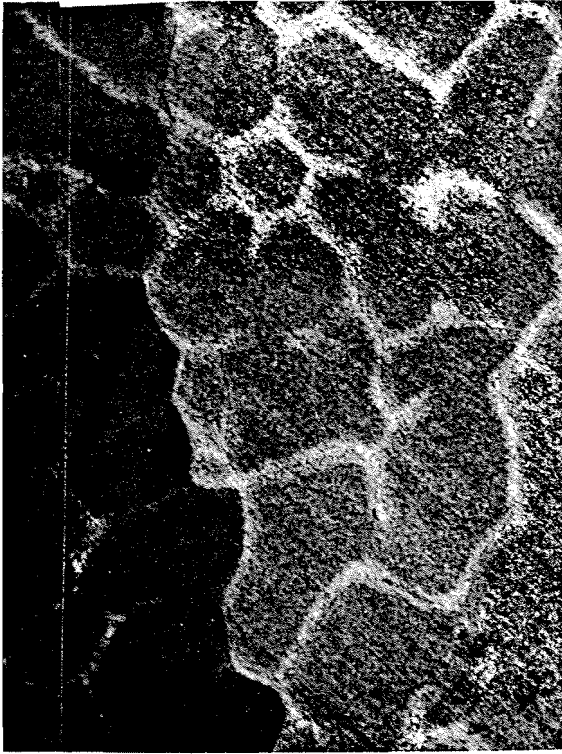


FIG. 8

Mag. 100x

DETAIL OF FIG. 7 SHOWING LARGE ANGLE
BOUNDARY RUNNING VERTICALLY BETWEEN TWO
LARGE GRAINS DISPLAYING INTERDENDRITIC
SEGREGATION.



Mag. 100x

FIG. 9

DETAIL OF FIG. 7 SHOWING SMALL EQUI-AXED
GRAINS WITHIN DENDRITIC SEGREGATION
PATTERN OF LARGE GRAINS.

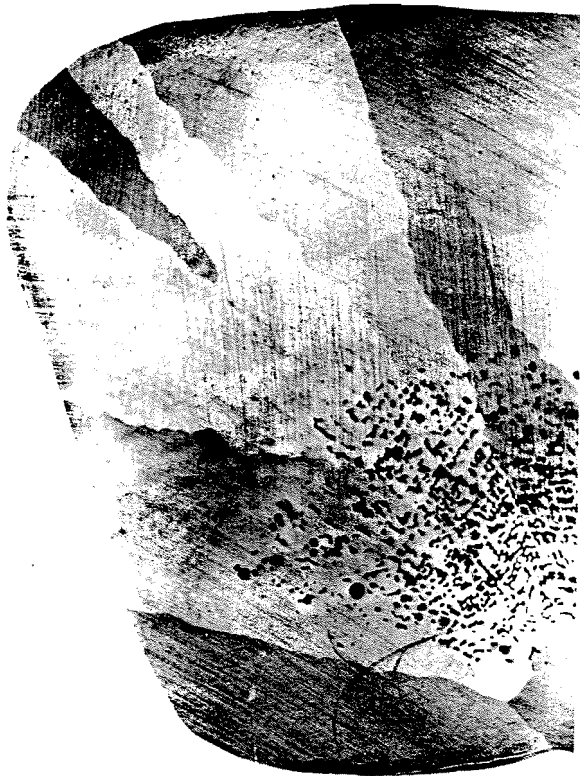


FIG. 10

Mag. 5x

PHOTOMICROGRAPH OF HALF VERTICAL SECTION SHOWING COARSE GRAIN-SIZE OF SAMPLE NUCLEATED AT 100°C UNDERCOOLING, REPRESENTATIVE OF SAMPLES NUCLEATED WITHIN THE RANGE 70°C TO 100°C UNDERCOOLING. THE DARK INTERDENDRITIC REGION IS POROSITY.



Mag. 5x

FIG. 11

PHOTOMICROGRAPH OF HALF VERTICAL SECTION SHOWING FINE-GRAIN STRUCTURE OF Cu - 4 WT % Fe SAMPLE (PERITECTIC COMPOSITION). QUENCHED IN WATER WHEN SOLIDIFICATION WAS COMPLETE.



FIG.12: DETAIL OF FIG. 11 SHOWING SHELL-LIKE NATURE OF PRIMARY IRON (DARK). A LARGE ANGLE BOUNDARY RUNS ACROSS THE PHOTOGRAPH.

Mag. 500x

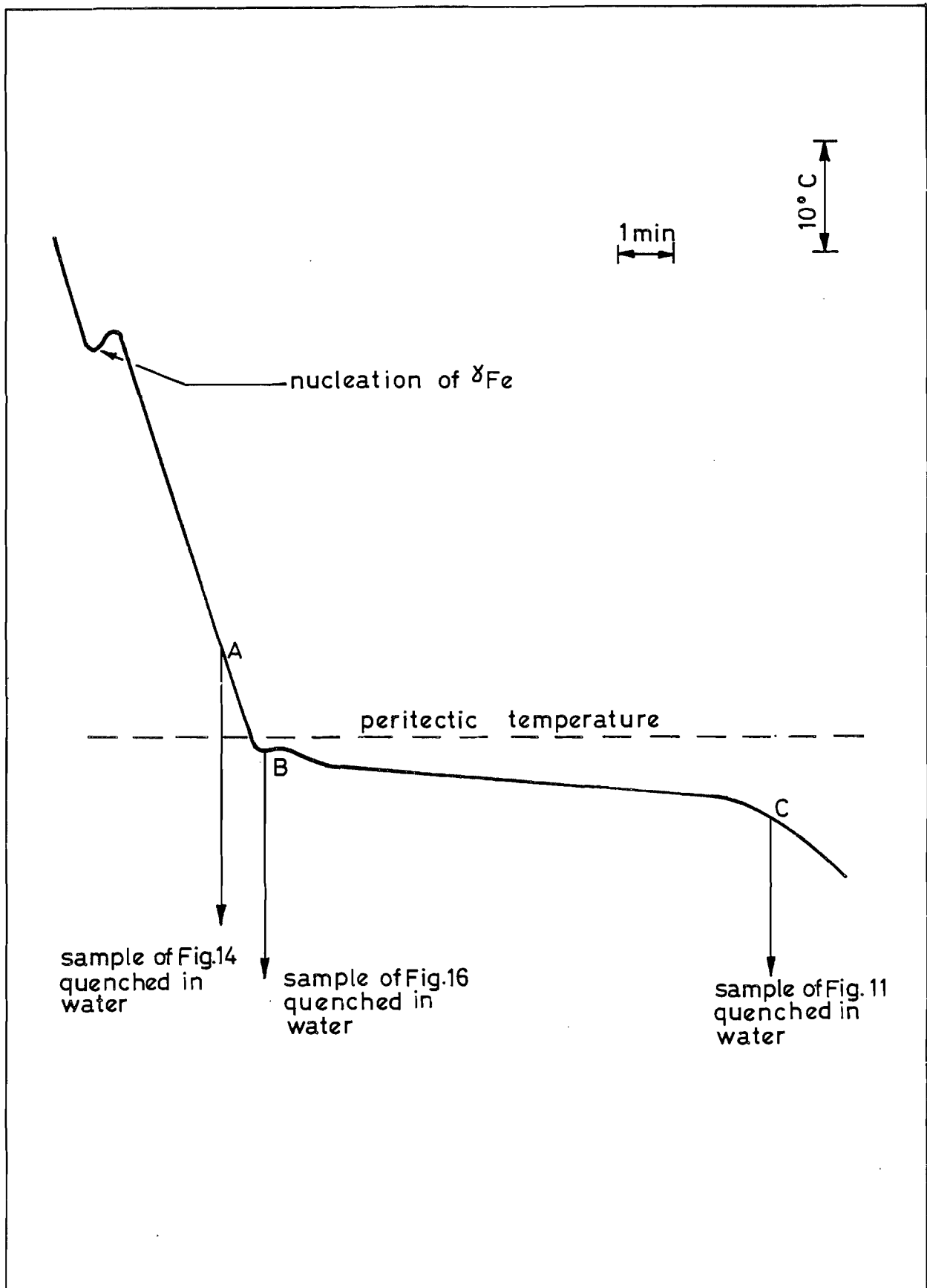


Fig.13: COOLING CURVE OF SAMPLE PERITECTIC COMPOSITION (Cu-4wt%Fe) SHOWING POSITIONS FROM WHICH THE SAMPLES OF Figs.14, 16 & 11 WERE QUENCHED IN WATER



FIG. 14

Mag. 5x

PHOTOMICROGRAPH OF HALF VERTICAL SECTION SHOWING MIXED GRAIN STRUCTURE OF SAMPLE OF PERITECTIC COMPOSITION QUENCHED FROM A TEMPERATURE ABOVE THE PERITECTIC TEMPERATURE (POINT A IN FIG. 13). NOTE THE FINER GRAINS IN THE CENTRAL PORTION OF THE SAMPLE.



Mag. 200x

FIG. 15

DETAIL OF FINE GRAIN-SIZE REGION OF FIG. 14 SHOWING FINE GRAINS SURROUNDING IRON DENDRITES (BLACK).



FIG. 16

Mag. 5x

PHOTOMICROGRAPH OF HALF VERTICAL SECTION SHOWING VARIABLE FINE-GRAIN STRUCTURE OF PERITECTIC SAMPLE QUENCHED FROM POINT B ON COOLING CURVE SHOWN IN FIG. 13.



Mag. 500x

FIG. 17

IRON DENDRITES (LIGHT) AT TOP SURFACE OF SAMPLE OF FIG. 15. A LARGE ANGLE BOUNDARY IS EVIDENT IN THE BOTTOM RIGHT-HAND CORNER.