A MICROSTRUCTURAL INVESTIGATION

OF A

DUPLEX CHILL CAST BRASS GRAIN REFINED

WITH ALUMINIUM AND BORON

BY

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SUMMARY

A 0.8wt% addition of aluminium masteralloy containing 4wt% boron was found to grain refine duplex brass cast into graphite moulds. The grain refined brass had three distinct grain zones: an outer zone of fine chill crystals, an inner zone of very fine equiaxed crystals and a zone of coarser equiaxed crystals between the two. An identical addition to a fully alpha brass showed no refining action while fully beta brass was moderately refined.

Using SEM and extraction replica techniques in the TEM the microstructure of all three brass compositions has been investigated. The marked grain refinement in the duplex brass was associated with the presence of a highly branched amorphous precipitate situated at the original beta grain boundaries. Crystalline second phase particles were observed in the fully alpha or fully beta alloys.

The composition of the amorphous and crystalline products has been investigated using WEDX and EELS analysis in the TEM. By combination of these techniques which are sensitive to light elements, an accurate analysis of the products was possible which proved them to be rich in boron and containing varying quantities of aluminium and oxygen. The boron glass was found to consist of; 88.7 wt% B, 6.3 wt% 0, 2.8 wt% Al with minor contents of Zn, Fe, S, Cu and P. By contrast the crystalline boron contained relatively more aluminium and less oxygen. An explanation of crystallinity of the boron products is made according to the composition.

Based upon this analysis and other considerations a novel grain refining mechanism is proposed which relies on the redistribution of boron solute ahead of the solidification front restricting the crystal growth.
Grateful acknowledgement is made to my supervisor at the University of Surrey, namely, Professor Goodhew for his advice in microstructural analysis and Dr. Tsakiropoulos for his guidance in the area of solidification and support in the writing of this thesis. Financial support was made available from the Science and Engineering Research Council and the London and Scandinavian Metallurgical Company (LSM). Mr. J. Cowell of LSM exercised much patience in teaching the "fire and brimstone" practices involved in making brass. Lastly, the help of P.M. Budd, D. Chescoe and the colleagues in the Microstructural Studies Unit at the University of Surrey is acknowledged.
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**List of Symbols Used**

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
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<tr>
<td>$\Delta G$</td>
<td>Free energy change associated with the formation of a spherical embryo (* of critical size).</td>
</tr>
<tr>
<td>$r$</td>
<td>Radius of an embryo (* of critical size).</td>
</tr>
<tr>
<td>$L$</td>
<td>Latent heat of fusion associated with the formation of a spherical embryo.</td>
</tr>
<tr>
<td>$\Delta T$</td>
<td>Melt Undercooling.</td>
</tr>
<tr>
<td>$T_e$</td>
<td>Equilibrium freezing temperature.</td>
</tr>
<tr>
<td>$\gamma$</td>
<td>Interfacial energy - subscripts sl, sc and lc denoting solid-liquid, solid-cluster and liquid-cluster.</td>
</tr>
<tr>
<td>$n_i$</td>
<td>Number of atoms in an embryo.</td>
</tr>
<tr>
<td>$n$</td>
<td>Effective total number of atoms per unit volume.</td>
</tr>
<tr>
<td>$k$</td>
<td>Boltzmann's constant.</td>
</tr>
<tr>
<td>$I$</td>
<td>Nucleation Rate.</td>
</tr>
<tr>
<td>$n_s$</td>
<td>Number of atoms in the liquid in contact with the solid.</td>
</tr>
<tr>
<td>$p$</td>
<td>Atomic jump directional probability function.</td>
</tr>
<tr>
<td>$\dot{\gamma}$</td>
<td>Atomic vibration frequency.</td>
</tr>
<tr>
<td>$\Delta G_d$</td>
<td>Free energy change associated with the transfer of an atom across the solid-liquid interface.</td>
</tr>
<tr>
<td>$\sigma$</td>
<td>Contact Angle.</td>
</tr>
<tr>
<td>$T_m$</td>
<td>Recorded freezing temperature.</td>
</tr>
<tr>
<td>$V$</td>
<td>Crystal Growth rate.</td>
</tr>
<tr>
<td>$D_l$</td>
<td>Liquid self diffusion constant.</td>
</tr>
<tr>
<td>$\nu$</td>
<td>Molecular Volume of the solid.</td>
</tr>
<tr>
<td>$g$</td>
<td>Diffuseness parameter to describe the solid-liquid interface.</td>
</tr>
<tr>
<td>Symbol</td>
<td>Definition</td>
</tr>
<tr>
<td>--------</td>
<td>------------</td>
</tr>
<tr>
<td>a</td>
<td>Step height due to the addition of one atom or molecule.</td>
</tr>
<tr>
<td>(k_o)</td>
<td>Equilibrium partition coefficient.</td>
</tr>
<tr>
<td>(C_s)</td>
<td>Equilibrium concentration of solute in the solid.</td>
</tr>
<tr>
<td>(C_l)</td>
<td>Equilibrium concentration of solute in the liquid.</td>
</tr>
<tr>
<td>(C_o)</td>
<td>Overall solute concentration.</td>
</tr>
<tr>
<td>(f_s)</td>
<td>Fraction solidified.</td>
</tr>
<tr>
<td>(C_s^*)</td>
<td>Solute concentration at the solid-liquid interface.</td>
</tr>
<tr>
<td>x</td>
<td>Distance from the solid-liquid interface.</td>
</tr>
<tr>
<td>(k')</td>
<td>Real partition coefficient.</td>
</tr>
<tr>
<td>G</td>
<td>Temperature gradient in the liquid.</td>
</tr>
<tr>
<td>m</td>
<td>Slope of the liquidus in the equilibrium phase diagram.</td>
</tr>
<tr>
<td>P</td>
<td>The Tarshis parameter.</td>
</tr>
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1. INTRODUCTION
Grain refinement is routinely practiced in the aluminium and magnesium casting industry by means of additions to the melt. In the early 1980s the London and Scandinavian Metallurgical Company (LSM), a world renowned producer of aluminium grain refiners, set out to develop and produce a copper grain refiner in response to requests from the copper casting industry. Copper casters and in particular manufacturers of brass water fittings were interested in casting thinner sections and hence saving on metal costs. This they presumed would be possible by the addition of a grain refiner. Initial experiments using boron and aluminium in a duplex brass resulted in a unique grain structure which contained some very fine grained areas. Detailed microstructural investigation of this refinement and particularly of the role played by the addition of boron was impeded by the difficulties associated with boron analysis.

Despite the numerous advances in sophisticated elemental microanalysis techniques in the TEM and SEM, accurate analysis of light elements and especially those lighter than oxygen remains difficult. Thin window and windowless energy dispersive X-ray analysers have recently been developed for this purpose along with other techniques such as EELS, LIMA and SIMS. The aim of this project was to use such advanced microstructural analysis techniques to investigate the boron and aluminium refinement of the duplex brass.

This thesis is separated into two main sections. The first covers the principles of solidification and the grain refinement of copper based alloys. The second section presents the experimental results and their discussion with particular emphasis given to the microstructure of the grain refined duplex brass. A possible grain refinement mechanism is also postulated. The list of all the casting experiments undertaken is given in the appendix. A part of the work has been published and a reprint is attached at the end.
2. THE BENEFITS OF GRAIN REFINING

The properties of castings are frequently contrasted with those of wrought products but the structure of wrought products can be much more freely modified than those of a cast product (1). Consequently the control of the cast grain size is important because of its major influence upon the chemical and physical properties of the casting (2).

The hot tearing susceptibility of a casting is reduced with decreasing grain size (3). Metz and Flemmings (4) attributed this to the fact that the development of strength and hot tearing susceptibility in a casting coincides with the formation of a solid dendrite network at about twenty five percent volume fraction solid. Below this fraction solid the casting has no strength and can accommodate any strain by rearrangement of or movement of the mass. As the fraction solid increases rearrangement becomes more difficult and was found to stop altogether in some dilute aluminium alloys with fifty percent fraction solidified. Conversely a fine grained casting (grain size about 10^{-3} m in diameter) did not start to develop any strength until forty percent fraction solidified and was thus less susceptible to hot tearing since it could accommodate better local strains without the formation of defects. Abdal Reihim and co-workers (5) were able to avoid the formation of continuous films of low strength tin, which segregated to the grain boundaries of an
aluminium-tin bearing alloy, by reducing the alloy grain size by means of an effective grain refiner.

The better feeding of a fine grained casting has also been found to lead to less shrinkage and a more even distribution of porosity (6). Further, the porosity in the fine grained ingots was smaller in size and more rounded in shape, thus having a less detrimental effect on the strength of the material. Cibula (7) however, points out that columnar structures do promote centre-line porosity, leaving a pressure-tight sound skin which is often desirable.

The studies of Frost and Ashby (8) indicate that the grain size of a material is important when considering the problem of creep. Grain boundaries act as barriers to low temperature dislocation glide but at high temperatures thermally activated dislocation climb can reduce grain boundary pile-up of dislocations. The lattice diffusion (Nabarro-Herring) type creep rate is quoted by Frost and Ashby as being inversely proportional to the square of the grain size while that of the grain boundary (Coble) diffusion creep is inversely proportional to the cube of the grain size. This phenomenon has been fully exploited in the aerospace industries where superalloys are produced in either directional columnar (9) or single crystal (10) state by careful control of the casting conditions (11) or by heat treatment subsequent to working (12) in order to avoid excessive creep of turbine blades at the high operating
temperatures of gas turbine engines.

The effect of grain size on the fatigue properties of metals has been reviewed by Armstrong (13). Grain boundaries block the propagation of slip bands which are produced in the fatigue process and fine grained castings are thus less sensitive to fatigue than coarse grained castings. This phenomenon has been widely exploited, again in the production of turbine blades, to produce components which have a fine grain size and are resistant to fatigue problems in the root section while the aerofoil is monocrystalline (11).

Hansen and Ralph (14) and Thompson and Backofen (15) were able to show a close agreement with the Hall-Petch relationship describing the increase in flow stress of pure copper with decrease in the grain size. These results are, however, in direct contrast with those of Coulton and Margolis (16) and French (17), who achieved better tensile results with coarse columnar structures rather than fine equiaxed grain structures in cast copper based alloys. This conflict is resolved by Coulton and Margolis (16) who state that a simple analysis of the tensile properties is incomplete without considering other reasons for the results such as porosity or shrinkage and that the course grain size may only be of secondary importance.

The results of Hansen and Ralph (14) and Thompson and Backofen (15) were achieved by subjecting highly mechanically
worked copper specimens to various annealing treatments to give a range of grain sizes from 150 to 8 micrometer diameters. Thus, these specimens would not be expected to show any effects of the casting in the tensile results. More recently Cowell and Nixon (18) have grain refined a selection of brasses (as described in Chapter 4) and carried out tensile tests on specimens machined from ingots of grain refined and non-grain refined alloys. These results are summarised in Table 2.1 and in all three alloys listed the grain refined alloys proved to have better tensile properties.

Thus, in conclusion it may be said that many of the improvements in grain refined copper based alloys derive from the improved casting properties leading to better feeding, shrinkage, porosity and hot tearing characteristics. The increased number of grain boundaries present in fine grained structures improves the fatigue resistant of a metal but may lead to excessive creep at high temperatures. The effect of grain refinement on the tensile properties of copper based alloys is less certain and the effects of increased grain boundary area may be secondary when compared to the improvements associated with the better casting properties of a fine grained material.
<table>
<thead>
<tr>
<th>ALLOY</th>
<th>GRAIN REFINEMENT</th>
<th>0.2% PROOF STRESS (MPa)</th>
<th>% ELONGATION</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Mean</td>
<td>Std Dev.</td>
<td>Mean</td>
</tr>
<tr>
<td>Alpha Brass</td>
<td>No</td>
<td>54</td>
<td>1.0</td>
</tr>
<tr>
<td>Cu Zn 30</td>
<td>Yes</td>
<td>76</td>
<td>1.0</td>
</tr>
<tr>
<td>Dezincification</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Resistant Brass</td>
<td>No</td>
<td>67</td>
<td>0.6</td>
</tr>
<tr>
<td>Cu Zn36 Pb2As</td>
<td>Yes</td>
<td>84</td>
<td>2.6</td>
</tr>
<tr>
<td>Two Phase</td>
<td>No</td>
<td>71</td>
<td>2.1</td>
</tr>
<tr>
<td>Leaded Brass</td>
<td>Yes</td>
<td>96</td>
<td>0.6</td>
</tr>
</tbody>
</table>

Table 2.1 The results of tensile tests on grain refined and non-grain refine brasses according to Cowell and Nixon (18)
3. SOLIDIFICATION OF METAL CASTINGS

This chapter reviews the processes by which solid metal is formed from the liquid and the influence of casting parameters upon these processes. Nucleation and growth are discussed in terms of the final ingot structure. The influence of alloying additions and classical grain refining procedures is also reviewed.

3.1 Nucleation

3.1.1 Homogeneous Nucleation

The classical theory of homogeneous nucleation was first developed for the case of liquid condensing from the vapour state (19, 20). Later work considered the precipitation of solid from the liquid phase and in solid state reactions (21, 22, 23). Since this work is concerned with the liquid to solid phase change only the former case will be discussed here.

According to the theory of homogeneous nucleation when liquid metal is cooled below its equilibrium freezing temperature, $T_e$, atoms may cluster together to form small solid particles. These are not necessarily stable (despite existing below $T_e$) since the free energy change associated with their formation contains both a volume term and a surface energy term due to the creation of a solid-liquid interface. (fig. 3.1).
3.1 Variation of free energy with nucleus size for the formation of a spherical nucleus (24).

Consequently there exists a critical radius below which the clusters are thermodynamically unstable. These clusters (also known as embryos) are thought to be constantly forming and re-dissolving in the melt. However, when their formation is accompanied by a net reduction of free energy, the nuclei become stable and homogeneous nucleation takes place (24, 25).

The overall free energy charge associated with the formation of a spherical embryo of radius \( r \) is given by:

\[
\Delta G = 4 \frac{1}{3} \pi r^3 \frac{L \Delta T}{T_e} + 4 \pi r^2 \psi_{SL} \tag{3.1}
\]

where \( L \) is the latent heat of fusion, \( \Delta T \) the undercooling and \( \psi_{SL} \) the solid-liquid interfacial energy. The value of the critical radius, \( r^* \), is

\[
r^* = \frac{2 \psi_{SL}}{L \Delta T} \tag{3.2}
\]
Volmer and Weber (26) and Frenkel (22) proposed that the probability of the formation of an embryo leading to a free energy change $\Delta G$ was proportional to $\exp\left(-\frac{\Delta G}{kT}\right)$ so that

$$n_1 = n \exp\left(-\frac{\Delta G}{kT}\right)$$  \hspace{1cm} (3.3)$$

with $n_1$ the number of atoms in the embryo. In eq (3.3) $n$ is effectively the total number of atoms per unit volume (149) and $k$ is Boltzmann's constant. For embryos of the critical size $r^*$ equation 3.3 is modified to

$$n_1^* = n \exp\left(-\frac{\Delta G^*}{kT}\right)$$  \hspace{1cm} (3.4)$$

with the value of $\Delta G^*$ given by (24)

$$\Delta G^* = \frac{16}{3} \pi \left(\frac{p_{sl}^3 r_e^2}{l^2 \Delta T^2}\right)$$  \hspace{1cm} (3.5)$$

Turnbull and Fisher (27) modified equations 3.4 to take into account the activation energy $\Delta G_d$ involved for the transfer of an atom across the solid-liquid interface. If it is assumed that clusters of the critical size grow and get removed from the system, then evaluation of the nucleation rate $I$ is reduced to a solid-liquid interface atomistic transfer problem. The nucleation rate is given as (28, 24, 25),

$$I = n_s \sigma n \exp\left(-\frac{\Delta G_d + \Delta G^*}{kT}\right)$$  \hspace{1cm} (3.6)$$

with $n_s$ the number of atoms in the liquid in contact with the
solid, $p$ is the probability of an atomic jump occurring in one direction and $\xi$ the atomic vibration frequency.

The classical theory of homogeneous nucleation has been criticised on several points (28, 29, 30). The surface energy term is considered to be the same as that for a macroscopic planar interface material. However, this may not be valid for nuclei containing about one hundred atoms. Furthermore, it has been suggested that a transition zone exists between the solid and liquid phases of approximately two to five atomic diameters in thickness and that the concept of surface energy is not appropriate in this case (21). The theory also proposes that the density of the nuclei is the same as that of the bulk liquid or solid even though a certain amount of free volume may be expected, since a number of vacant lattice sites could occur in a just nucleated and growing solid cluster of atoms (29). Lothe and Pound (31) examined the possibility of a nucleus having additional degrees of freedom, such as rotation. Reiss and Katz (32, 33) showed that the original inconsistencies which gave rise to the argument of the additional degrees of freedom are caused by the fluctuation of the centre of a cluster which becomes important only for large nuclei.

3.1.2 Heterogeneous Nucleation

The classical theory of homogeneous nucleation assumes that collisions and interactions between embryos and atoms can occur with equal probability anywhere in the liquid. This, however, is considered unlikely in practice and instead
heterogeneous nucleation takes place. In the latter case any interactions between an embryo and a foreign substrate and their effect on the stability of the embryo are very important. As before, the condition which must be attained for an embryo to become a stable nucleus is that its radius must exceed a certain critical value. This can be accomplished if the embryo forms a stable cap on the surface of substrate fig. 3.2. Here the periphery of the embryo is stable if the total free energy of the system is unchanged by the displacement of points A and A'. This occurs when

\[ \psi_{sl} - \psi_{sc} = \psi_{lc} \cos \theta \]  

(3.7)

where the subscripts sl, sc and lc denote the substrate-liquid, substrate-cluster and liquid-cluster interfaces respectively.

Fig. 3.2 Formation of a Nucleus on a Substrate.
The critical free energy $\Delta G^*_{\text{het}}$ required to form a stable cap on a substrate is less than $\Delta G^*_{\text{hom}}$,

$$\Delta G^*_{\text{het}} = \Delta G^*_{\text{hom}} f(\theta)$$  \hspace{1cm} (3.8)

where

$$f(\theta) = (2 + \cos \theta)(1 - \cos \theta)^2$$  \hspace{1cm} (3.9)

As the contact angle $\theta$ becomes small, $f(\theta)$ approaches zero, the critical nucleus becomes a very thin disc on a substrate (fig.3.3) and $\Delta G^*_{\text{het}}$ also approaches zero (34)

![Graph showing variation of $f(\theta)$ with $\theta$, the contact angle](image)

Fig. 3.3 Variation of $f(\theta)$ with $\theta$, the contact angle (25)

Equation 3.6 is then modified to give the heterogeneous nucleation rate (24).

$$-I_{\text{het}} = n_s^* \dot{\rho} n \exp(-\frac{f(\theta) \Delta G^* + \Delta G_d^*}{kT})$$ \hspace{1cm} (3.10)

where now $n_s^*$ is the number of atoms in the liquid in contact with the solid substrate. Thus, $I_{\text{het}}$ is proportional to the surface area of the substrate which catalyses the phase change reaction. The size and
distribution of any heterogeneous nucleating additions is therefore very important in determining the heterogeneous nucleation rate (21).

3.1.3 Nucleation in Liquid Metals

Equation 3.6 can also be written as (28):

\[ I = n \left( \frac{kT}{h} \right) \exp \left( \frac{\Delta G^* + \Delta G^*}{kT} \right) \] (3.11)

where \( h \) is Planck's constant. In equation 3.11 \( n \) is about \( 10^{28-29} \) m\(^{-3} \) and \( kT/h \) is \( 10^{13} \) s\(^{-1} \). The value of \( \Delta G^* \) is unknown but Frenkel (22) estimated it as being equal to the activation energy for viscous flow of a fluid since both processes occur by the same mechanism. This approximates \( \exp \left( \frac{-\Delta G^*}{kT} \right) \) to \( 10^{-2} \) for the solid-liquid transformation in metals. Equation 3.11 then simplifies to

\[ I = 10^{39} \exp \left( \frac{\Delta G}{kT} \right) \text{ m}^{-3} \text{s}^{-1} \] (3.12)

and substitution of eq. (3.5.) gives

\[ I = 10^{39} \exp \left[ \frac{16 \mu_{cal} \gamma^2 \xi^2}{3t_1^2 \Delta T^2 kT} \right] \] (3.13)

Turnbull investigated the freezing of liquid metals (35). Since their crystallisation could be influenced by the presence of impurities he divided the liquid into fine droplets which were separated by a thin inert chemical film. Thus he could ensure that many droplets could be free of
impurities and expected that crystallation of the majority of the droplets would be nucleated homogeneously or heterogeneously by the surface film.

A thorough study was made of the solidification kinetics of mercury droplets. Nucleation undercoolings were found to vary strongly with the surface film as shown in fig. 3.4 (35). The greatest undercoolings were observed in droplets covered with mercury laurate and it was established that in this case the nucleation frequency was proportional to the droplet volume, indicating homogeneous nucleation. In the other systems investigated the nucleation frequency was proportional to the surface area of the droplet, indicating a heterogeneous nucleation path.

Analysis of the nucleation rates (21) gave a value of the pre-exponential factor ($10^{46} \text{ m}^{-3} \text{ s}^{-1}$) which was higher than the predicted value ($10^{39} \text{ m}^{-3} \text{ s}^{-1}$). This difference (a factor of $10^7$) was too great to be accounted for by experimental error and was attributed to a possible temperature dependence of the entropy of fusion. It was also proposed that the structure of the mercury nucleus could be different from that of bulk mercury leading to a lower melting temperature.

Miyazawu and Pound (36) studied solidification of gallium droplets dispersed in various organic liquids and concluded that their results were compatible with homogeneous
nucleation. However, they calculated a pre-exponential factor of about $10^{45}$, which is six orders of magnitude higher than the value in equation 3.13. This difference was attributed to the temperature dependence of the heat capacity (gallium undercooled by 100K) and to the temperature dependence of $\beta_{sl}$. It was also pointed out that the estimated value of $\Delta G^*d$, could lead to an error by a factor of ten.

Turnbull and Cech (37), showed that under their conditions the maximum amount of undercooling was $\Delta T = 0.18T_m$, where $T_m$ is the melting temperature in degrees kelvin. From these results (35) Turnbull (38) was able to calculate the surface free energy, $\gamma_{sc}$, for various metals, see table 3.1. However, as will be shown below this value of $T$ has been exceeded in more recent experiments where alternative experimental techniques have been developed to measure the interfacial energy (39).

Glicksman and Childs (40) measured the undercooling of liquid tin solidified under vacuum in a pyrex crucible and the effect which certain substrates had on the magnitude of the nucleation undercooling. The contact angle $\theta$ was also estimated and this gave a measure of the nucleating potency of a particular heterogeneous nucleation catalyst. Some of the nucleation rate - undercooling curves observed are shown in fig. 3.4. It was found that the values for metals were the lowest observed, tin showing no recordable undercooling.
Non metals (oxides, carbides and sulphides) showed higher undercoolings and consequent contact angles, as in Table 3.2. Furthermore, distinct crystal orientations of the same substrate material resulted in lower undercoolings than other less favourable orientations. For example, the prismatic plane of yttrium resulted in a 6K undercooling whereas, the basal plane resulted in 8K.

<table>
<thead>
<tr>
<th>Metal</th>
<th>Maximum Undercooling (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aluminium</td>
<td>130</td>
</tr>
<tr>
<td>Manganese</td>
<td>308</td>
</tr>
<tr>
<td>Iron</td>
<td>295</td>
</tr>
<tr>
<td>Cobalt</td>
<td>330</td>
</tr>
<tr>
<td>Nickel</td>
<td>319</td>
</tr>
<tr>
<td>Copper</td>
<td>236</td>
</tr>
<tr>
<td>Palladium</td>
<td>232</td>
</tr>
<tr>
<td>Silver</td>
<td>227</td>
</tr>
<tr>
<td>Platinum</td>
<td>370</td>
</tr>
<tr>
<td>Gold</td>
<td>230</td>
</tr>
<tr>
<td>Lead</td>
<td>80</td>
</tr>
<tr>
<td>Gallium</td>
<td>76</td>
</tr>
<tr>
<td>Germanium</td>
<td>227</td>
</tr>
<tr>
<td>Tin</td>
<td>118</td>
</tr>
<tr>
<td>Antimony</td>
<td>135</td>
</tr>
<tr>
<td>Mercury</td>
<td>77</td>
</tr>
<tr>
<td>Bismuth</td>
<td>90</td>
</tr>
</tbody>
</table>

Table 3.1 Summary of the results of the undercooling experiments of Turnbull (41)

This they proposed was due to the fact that the lattice spacing of the prismatic phase was closer to that of pure tin than was the lattice spacing of the basal plane.
Fig. 3.4 Schematic plot of nucleation frequency against supercooling for various values of the equilibrium contact angle \( \sigma \).

<table>
<thead>
<tr>
<th>Substrate</th>
<th>Form</th>
<th>( \Delta T ) (K)</th>
<th>( \sigma ) (deg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tin</td>
<td>Monocrystal</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Platinum</td>
<td>Polycrystal</td>
<td>4</td>
<td>17.0</td>
</tr>
<tr>
<td>Yttrium</td>
<td>Monocrystal</td>
<td>6</td>
<td>21.5</td>
</tr>
<tr>
<td>Silver</td>
<td>Polycrystal</td>
<td>7</td>
<td>23.0</td>
</tr>
<tr>
<td>TiC</td>
<td>Monocrystal</td>
<td>15</td>
<td>34.5</td>
</tr>
<tr>
<td>MoS</td>
<td>Monocrystal</td>
<td>17</td>
<td>37.0</td>
</tr>
<tr>
<td>Aluminium</td>
<td>Polycrystal</td>
<td>18</td>
<td>38.0</td>
</tr>
<tr>
<td>SiC</td>
<td>Monocrystal</td>
<td>&gt;26</td>
<td>&gt;46.0</td>
</tr>
<tr>
<td>Al(_2)O(_3)</td>
<td>Monocrystal</td>
<td>&gt;28</td>
<td>&gt;48.0</td>
</tr>
<tr>
<td>CeS</td>
<td>Polycrystal</td>
<td>&gt;30</td>
<td>&gt;50.0</td>
</tr>
<tr>
<td>MgO</td>
<td>Monocrystal</td>
<td>&gt;31</td>
<td>&gt;51.0</td>
</tr>
<tr>
<td>Graphite</td>
<td>Textured</td>
<td></td>
<td></td>
</tr>
<tr>
<td>&quot;</td>
<td>Polycrystal</td>
<td>&gt;33</td>
<td>&gt;53.0</td>
</tr>
</tbody>
</table>

Table 3.2 Summary of the Catalysis Experimental results of Glicksman and Childs (40)

Southin and Chadwick (42) studied nucleation in alloys which were heat-treated so as to produce spheres of low melting point material in a higher melting point matrix. Higher undercoolings than those of Turnbull and Cech (37) were estimated while the lowest undercoolings were observed in couples (matrix-droplet) of similar crystal structure.
Some of the most significant recent experiments on the undercooling of liquid metal are the recent works of Perepezko and co-workers (43, 44, 45, 46). Liquid metal droplets are dispersed in either an organic carrier fluid or a molten salt carrier flux mixture as illustrated in fig. 3.5(a). Perepezko proposes that the limit of undercooling of the droplet depends on either the catalytic nature of the surface coating or the onset of homogeneous nucleation (43). Since surface coatings of a non-crystalline type will not tend to wet the liquid phase and discourage catalysis of heterogeneous nucleation, Perepezko expected that such methods would facilitate significant undercoolings.

Fig. 3.5 Liquid Undercooling Methods after Perepezko (43).

Using differential thermal analysis Perepezko measured undercoolings far greater than those recorded by Turnbull and
Cech (37) for the same material, as shown in Tables 3.3 and 3.1.

<table>
<thead>
<tr>
<th></th>
<th>Maximum Undercooling (K)</th>
<th>$\Delta T/ T_m$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aluminium</td>
<td>160</td>
<td>0.17</td>
</tr>
<tr>
<td>Antimony</td>
<td>210</td>
<td>0.23</td>
</tr>
<tr>
<td>Bismuth</td>
<td>227</td>
<td>0.41</td>
</tr>
<tr>
<td>Lead</td>
<td>153</td>
<td>0.26</td>
</tr>
<tr>
<td>Mercury</td>
<td>88</td>
<td>0.38</td>
</tr>
<tr>
<td>Tin</td>
<td>187</td>
<td>0.37</td>
</tr>
<tr>
<td>Cadmium</td>
<td>110</td>
<td>0.19</td>
</tr>
<tr>
<td>Indium</td>
<td>110</td>
<td>0.26</td>
</tr>
</tbody>
</table>

Table 3.3 Maximum Undercoolings recorded by Perepezko (43)

Almost all undercoolings are well below the $\Delta T/T_m$ ratio of 0.18 proposed by Turnbull and suggested as corresponding to the onset of homogeneous nucleation. Turnbull therefore did not achieve homogeneous nucleation in his experiments. Graves, Shong and Perepezko tried a containerless solidification technique of the type shown in fig. 3.5(e) to study the solidification of alloy droplets in free flight. By using the relationship between undercooling and lamellar spacing they estimated undercoolings of 0.23 $T_M$ for an In-Sb-Sb alloy and 0.35 for a Ni-Nb alloy.
3.2 Growth

Growth of a crystal from the liquid can be influenced by many factors. These will be considered primarily in terms of how the undercooling of a pure liquid melt can affect the growth rate.

Some of the earliest and most important work undertaken on crystal growth was that of Stranski (46, 47) who proposed that atoms joining a solid interface can attach themselves at three different sites, fig. 3.6(a), occurring in the presence of steps on a surface. Stranski found evidence for this mode of growth in his work on the growing of single cadmium crystals from the vapour phase (47). According to his mechanism growth continued in a lateral manner and required that another favourable nucleation site is created for crystal growth to continue perpendicular to the surface, Fig. 3-6(b)

![Fig. 3.6](image)

Fig. 3.6 (a) Atomic addition at a favourable site on a surface according to Stranski (46), (b) Growth perpendicular to the crystal surface.
Growth mechanisms were therefore not continuous and it was not until Frank (48) proposed a screw dislocation mechanism that a theory was developed to explain the marked difference between observed and theoretical growth rates, whereby growth could take place without the necessity for the constant replenishing of favourable growth sites. This growth mechanism is illustrated in fig. 3.7 and the spiral stepped crystal surface associated with it has been widely reported, particularly by Verma (49) in his work with silicon carbide crystals.

Fig. 3.7 The End of Screw dislocation offering favourable bonding sites (48).
Cahn (50) proposed that the lateral and screw dislocation growth mechanisms could be characterised by the driving force required to promote the specific type of growth. The driving force for screw dislocation type growth was found to be significantly lower than that required to bond an atom onto an atomically smooth surface to permit lateral growth. The diffuseness parameter, \( g \), was introduced to describe the solid-liquid interface. A diffuse interface was one where the transition from liquid to solid took place over several atomic diameters. For extremely diffuse interfaces the critical driving force for growth by the attachment of atoms will be so small that any measurable driving force would exceed it.

Cahn, Hill and Sears (51) showed that under conditions for special type growth where the driving force for crystallisation is small and the interface is sharp (i.e. \( g \) is small) the growth rate \( V \) is given by

\[
V = \frac{\frac{6}{5} D_l L \Delta T^2}{4 \pi \gamma^2 k T \beta |S| V} \frac{1 + 2\eta^2}{g} \tag{3.14}
\]

where \( V \) is the growth rate of the solid, \( D_l \) is the liquid self diffusion coefficient, \( L \) is the latent heat of fusion per mole, \( \beta \) is the molecular volume of the solid and \( \eta \) is a constant related to the jump distance in the liquid state.
Under conditions where the driving force for growth is large, the situation in fig. 3.6(b), the growth rate is given by (51)

\[ V = \frac{6D_i \Delta T}{a k T e^2} \]  

(3.15)

where \( a \) is the step height due to the addition of one atom or molecule. There exists a transitional zone between the two growth forms, fig. 3.8.

Fig. 3.8 Predicted growth rate curve for a surface will on emergent dislocation after Cahn Hillig and Sears (51).
In the absence of lateral growth sites or screw dislocations, a two-dimensional nucleation is possible when a sufficiently large number of atoms attach to the surface at any one time to form a cluster or disc, which can be stable to grow, as shown in Fig. 3.9.

Fig. 3.9. Surface step created by surface nucleation (52).

This process is similar to heterogeneous nucleation since the larger the disc radius the more stable the configuration becomes. Hence growth kinetics are dictated primarily by the nucleation rate of these critical size discs and the growth rate can be expressed

\[ V = C_1 D_1 \exp\left(-\frac{C_2}{AT}\right) \quad (3.16) \]

where \( C_1 \) and \( C_2 \) are constants.
However, there is little experimental evidence for this growth mechanism (53), which is expected to operate at relatively high undercoolings, Fig. 3.10.

![Diagram showing growth rate vs. supercooling](image)

Fig. 3.10. The influence of interface undercooling on the growth rate and mechanism for atomically rough and smooth interfaces (24).

Other growth mechanisms have been proposed for specific materials such as the twin type growth by silicon observed in aluminium silicon alloys (54). Direct measurements of growth velocities are difficult because of the opacity of metals and researchers have had to model crystal growth using transparent solutions (55, 56, 57). Colligan and Boyles (58) used two optical films to record recalescence in a solidifying nickel melt at undercoolings of 20-300K by the application of a small nickel rod to the surface. By
positioning the probes at a specific distance, one near the top surface and the other near the bottom of the melt, they were able to compare the probe results with high speed photographic measurements of the rate of advance of the solidification front across the upper surface of the ingot. These results give a dependence of growth on undercooling of the form

\[ V = 0.28 \Delta T^{1.8} \]  \hspace{1cm} (3.17)

Kramer and Tiller (59) and Rigney and Blakely (60) studied the crystal growth of tin using a 'thermal wave' technique. Single crystals of tin were prepared from zone refined tin and sealed in a glass tube containing thermocouples along the length. The tube was heated in such a way as to set up a temperature gradient along the tube with the solid-liquid interface lying centrally between the two ends. By applying a thermal wave to the hotter end, the s-l interface was seen to move during heating and cooling and the advance of the interface was measured by the thermocouples. However, the results of the two groups, using the same technique and material, differ markedly. Rigney and Blakely (60) found that:

\[ V = u_1 \Delta T \]  \hspace{1cm} (3.18)

where \( u_1 \) is a constant equal to 0.007, 0.008 and 0.019 in the \(<332>\), \(<103>\) and \(<110>\) crystallographic directions.
respectively. Kramer and Tiller (61) found:

\[ V = u_2 \Delta T^2 \]  

(3.19)

where in this case \( u_2 \) lies between 35 and 65, thus suggesting not only a large difference in the values of the constants but also the dependence of the growth velocity on undercooling. In discussing the Rigny and Blakely paper, Tiller (43) does draw attention to the possibility of convection currents leading to inaccuracies and also that according to equation (3.18) an undercooling of 50K is required to attain a crystal growth velocity of 1 cm/sec.

In a more recent work Kobayashi and Konickawa (62) placed thermocouples along a directionally solidified melt to measure the recalescence. They studied five metals and their results, along with other values reported in the literature are given in Table 3.5. It is worth noting not only the difference in the results for the same metal by different researchers but also the variation in the form of the growth velocity - undercooling relationship. The relationship reported by Kobayashi and Konickawa is plotted in Fig. 3.11. Despite these inconsistencies in the literature, it can be said that the growth rate of s-l interface increases with \((\Delta T)^n\) where \( n \) varies between 1.5 and 2.0, thus approaching the relationship predicted by a spiral growth mechanism.
<table>
<thead>
<tr>
<th>Metal</th>
<th>Crystal Structure</th>
<th>Undercooling min/max (K)</th>
<th>Growth rate x 10^-2 m/s</th>
<th>Work</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hg</td>
<td>Rhombic</td>
<td>-</td>
<td>&gt;9.2(ΔT)</td>
<td>Reviewed</td>
</tr>
<tr>
<td>Ga</td>
<td>Orthorhombic</td>
<td>0.48/0.75</td>
<td>7×10^3 exp(-3900/TAT)</td>
<td>&quot;</td>
</tr>
<tr>
<td>Ga</td>
<td>-</td>
<td>1.1/1.5</td>
<td>5.4×10^5 exp(-11000/TΔT)</td>
<td>&quot;</td>
</tr>
<tr>
<td>Ga</td>
<td>-</td>
<td>0.05/0.25</td>
<td>0.42(ΔT)^2</td>
<td>&quot;</td>
</tr>
<tr>
<td>Ga</td>
<td>-</td>
<td>0/2.8</td>
<td>5.3 (ΔT)</td>
<td>&quot;</td>
</tr>
<tr>
<td>Rb</td>
<td>bcc</td>
<td>-</td>
<td>&gt;5.4 (ΔT)</td>
<td>&quot;</td>
</tr>
<tr>
<td>K</td>
<td>bcc</td>
<td>-</td>
<td>&gt;4.1 (ΔT)</td>
<td>&quot;</td>
</tr>
<tr>
<td>In</td>
<td>fc tetragonal</td>
<td>-</td>
<td>&gt;11 (ΔT)</td>
<td>&quot;</td>
</tr>
<tr>
<td>Sn</td>
<td>Tetragonal</td>
<td>0.4/10</td>
<td>0.25 (ΔT)^2</td>
<td>&quot;</td>
</tr>
<tr>
<td>Sn</td>
<td>Tetragonal</td>
<td>2/15</td>
<td>0.04 (ΔT)^1.8</td>
<td>&quot;</td>
</tr>
<tr>
<td>Sn</td>
<td>Tetragonal</td>
<td>0.006/0.06</td>
<td>50 (ΔT)^2</td>
<td>&quot;</td>
</tr>
<tr>
<td>Sn</td>
<td>Tetragonal</td>
<td>0.003/0.5</td>
<td>0.007 (ΔT)</td>
<td>&quot;</td>
</tr>
<tr>
<td>Sn</td>
<td>Tetragonal</td>
<td>0.003/0.5</td>
<td>0.019 (ΔT)</td>
<td>&quot;</td>
</tr>
<tr>
<td>Sn</td>
<td>Tetragonal</td>
<td>0.2/0.5</td>
<td>0.2 (ΔT)^2</td>
<td>&quot;</td>
</tr>
<tr>
<td>Sn</td>
<td>Tetragonal</td>
<td>&gt;0/0.6</td>
<td>0.067 (ΔT)^2</td>
<td>&quot;</td>
</tr>
<tr>
<td>Sn</td>
<td>Tetragonal</td>
<td>9/17</td>
<td>0.28 (ΔT)^1.74</td>
<td>&quot;</td>
</tr>
<tr>
<td>Pb</td>
<td>fcc</td>
<td>2.5/6</td>
<td>0.5 (ΔT)^1.5</td>
<td>&quot;</td>
</tr>
<tr>
<td>Bi</td>
<td>Rhombic</td>
<td>0.4/1.6</td>
<td>0.012 (ΔT)^1.7</td>
<td>&quot;</td>
</tr>
<tr>
<td>Cd</td>
<td>Cph</td>
<td>-</td>
<td>&gt;5.5 (ΔT)</td>
<td>&quot;</td>
</tr>
<tr>
<td>Ni</td>
<td>fcc</td>
<td>20/200</td>
<td>2.8 (ΔT)^1.8</td>
<td>&quot;</td>
</tr>
<tr>
<td>Ni</td>
<td>fcc</td>
<td>&gt;0/175</td>
<td>14 (ΔT)^2</td>
<td>&quot;</td>
</tr>
<tr>
<td>Co</td>
<td>fcc</td>
<td>15/250</td>
<td>0.16 (ΔT)^2</td>
<td>&quot;</td>
</tr>
<tr>
<td>Cu</td>
<td>fcc</td>
<td>15/200</td>
<td>0.53 (ΔT)^1.8</td>
<td>&quot;</td>
</tr>
<tr>
<td>Ag</td>
<td>fcc</td>
<td>15/100</td>
<td>0.97 (ΔT)^1.7</td>
<td>&quot;</td>
</tr>
<tr>
<td>Bi</td>
<td>Rhombic</td>
<td>6.7/24</td>
<td>0.022 (ΔT)^1.67</td>
<td>Authors'</td>
</tr>
<tr>
<td>Sb</td>
<td>Rhombic</td>
<td>3/62</td>
<td>0.94 (ΔT)^1.43</td>
<td>&quot;</td>
</tr>
<tr>
<td>Te</td>
<td>Hexagonal</td>
<td>11.5/42.5</td>
<td>0.0025 (ΔT)^2.87</td>
<td>&quot;</td>
</tr>
<tr>
<td>Sn</td>
<td>Tetragonal</td>
<td>10/40</td>
<td>0.22 (ΔT)^1.81</td>
<td>&quot;</td>
</tr>
<tr>
<td>Pb</td>
<td>fcc</td>
<td>0.5/1.6</td>
<td>2.3 (ΔT)^1.65</td>
<td>&quot;</td>
</tr>
</tbody>
</table>

Table 3.4 The measured growth rate data for pure metals by various researchers as summarised by Kobayashi and Komickawa (62).
Fig. 3.11  The growth rate - undercooling relationships measured by Kobayashi and Konickawa (62)

3.3 Solute Redistribution During Solidification

In discussing the redistribution of solute during solidification it is better to consider the simplest situation of a planar solid-liquid interface and then to add constraints to account for the type of freezing conditions normally encountered. Of great importance is the difference in solubility of one species between the solid and liquid
phases. The equilibrium partition coefficient, $k_0$, is expressed as

$$k_0 = \frac{C_s}{C_l} \quad (3.20)$$

where $C_s$ and $C_l$ are the equilibrium concentrations of solute in the solid and liquid phases respectively.

Scheil (63) and Pfann (64) considered the situation where there is effectively no diffusion within the solid phase and perfect mixing in the liquid and showed that the composition of the solid at the s/l interface, $C^*_s$, is given by

$$C^*_s = k_0 C_0 (1 - f_s)^{k_0^{-1}} \quad (3.21)$$

where $f_s$ is the fraction solidified and $C_0$ is the alloy concentration. Equation 3.21 is known as the Scheil equation.

Scheil's analysis considers that diffusion in the liquid is complete. Tiller et al (65) proposed that any solute rejected from the advancing solid-liquid interface would not diffuse throughout the liquid but would form an enriched solute layer ahead of the interface. The solute concentration profile of such a layer is shown in Fig. 3.12b.
The authors were able to show that the concentration profile of such a layer under steady state conditions is given by

\[ c_I = c_0 \left[ 1 + \frac{1 - k_0}{k_0} \exp \left( \frac{Vx}{D_\perp} \right) \right] \]  

(3.22)

where \( V \) is the rate of advance of the interface, \( D_\perp \) is the
diffusion coefficient of the solute in the liquid and \( x \) is the distance from the interface. The concentration of solute in the liquid decays exponentially with distance and a characteristic distance \( \delta \) in Fig. 3.12(b) is defined by \( D/V \), the distance over which the concentration falls to \( 1/e \) of its initial value. The decrease in the value of the characteristic distance with growth rate is shown in Fig. 3.13 where the diffusion coefficient is taken as \( 5 \times 10^{-9} \) \( \text{m}^2/\text{s} \) (65).

![Graph of characteristic distance vs. rate of growth](image)

Fig. 3.13 Characteristic distance \( D/V \) of the solute distribution in the liquid as a function of growth rate \( V \).

Burton Prim and Slichiler (67) argued that since there is always some solvent convection within the liquid ahead of the
interface, the value of the partition coefficient in practice is seen to be between \( k_0 \) and unity. The real value, the partition coefficient of \( k' \) is given by

\[
k' = \frac{k_0}{k_0 (1-k_0) \exp\left(-\frac{V}{D_1}\right)}
\]  

and it is this value that should be used in equation 3.23.

The major implication for the stability of a s-l interface is associated with the build up of solute under ideal conditions since it is possible to predict the liquidus temperature of the layer from the equilibrium phase diagram as in Fig. 3.14(a). The equilibrium liquidus can then be plotted as a function of distance Fig. 3.14(c) and (d). The liquidus rises due to the high solute content and can be compared with the actual temperature gradient in the liquid. Fig. 3.14(c) shows a stable s/l interface whereas in (d) the actual gradient is below the liquidus temperature for a certain distance. Tiller, Jackson Rutter and Chalmers (65) were able to show that under conditions of no solid diffusion and no liquid convection such undercooling would occur if:

\[
\frac{G}{V} \ll \frac{mC_0 (1-k_0)}{D_1 k_0}
\]  

where \( m \) is the slope of the liquidus in the equilibrium phase diagram and \( G \) is the temperature gradient in the liquid.

Thus, constitutional supercooling (as it is now known) is favoured by large values of \( V \) and \( C_0 \) and by small values of \( G \).
and $k_0$. It may be expected that under favourable conditions relatively high constitutional supercoolings may be attained. However, in practice a very small amount of undercooling is sufficient to set up instabilities which lead to departures from the steady state conditions governing the advance of a planar s-1 interface. A low growth rate in a relatively pure single phase alloy may result in a planar solid-liquid interface. With increasing growth rate the s-1 interface becomes unstable and under further increase in the growth

Fig. 3.14 Constitutional Supercooling in alloy solidification (a) Phase diagram (b) Solute enriched layer ahead of solid-liquid interface (c) stable interface (d) Unstable interface. (66).
rate the cells branch and dendrites are formed (68).
Cellular or dendritic solidification is then accompanied by segregation of solute in the intercellular regions.

The transition from a planar to a cellular interface has been further analysed by Mullins and Sekerka (68). The constitutional supercooling criterion does not give any information about the size of perturbations which may develop when a planar interface becomes unstable nor does it take into account any surface tension effects.

Mullins and Sekerka (68) considered an interface with a sinusoidal perturbation having a very small, time dependent amplitude and the conditions under which such perturbations would enlarge or decay. They were able to show the existence of a critical wavelength \( \lambda_{\text{crit}} \) of perturbation below which the interface was stable and the perturbation would decay. Perturbations of wavelength \( \lambda_{\text{crit}} \) or above will grow, the wavelength exhibiting the highest rate of development becoming the most dominant. This analysis also predicts the existence of 'absolute stability' of an interface at high growth rates such as those encountered in rapid solidification processing.

The applicability of classical solute redistribution to dendritic solidification was investigated by Brody and Flemmings (69) who considered the mass flow of solute in and out of a volume element containing the solid liquid interface
of a dendritic array. In their analysis the effects of diffusion in the solid after freezing were included and an accurate prediction was made of the amount of non-equilibrium eutectic found in some aluminium copper alloys as measured by microprobe analysis (70) thus confirming that the Scheil equation, (equation 3.25) describes accurately solute redistribution between the solute dendrite arms. More importantly, by measuring the undercooling at the dendrite tips of a directionally solidified alloy, they were able to show that the solute build up at the tips was negligible for growth rates of $5 \times 10^{-6}$ to $5 \times 10^{-5}$ m s$^{-1}$.

This has been explained by Verhoeven (71) as being due to the lateral diffusion of solute into the interdendritic regions.

Clyne and Kurz (72) showed the Brody-Flemmings analysis to be valid only when there is no appreciable back diffusion. However, when interstitial alloys, such as steels, are considered the higher diffusivity requires the back diffusion of the solute to be taken into account thus resulting in solidification closer to the conditions of the lever rule type.
3.4 Ingot Structure

The typical ingot structure, as shown in Fig. 3.15, has three distinctive zones. The outer chill zone consists of fine equiaxed randomly-orientated crystals which are thought to be formed as the molten metal initially comes into contact with the mould wall which offers many favourable heterogeneous nucleation sites (73). The number of nucleated crystals depends upon the effectiveness of the mould wall as a nucleant. Thus, a rough wall will produce more chill crystals and a mould heated to near the liquidus temperature...
may produce no chill zone at all (24, 25).
The columnar zone is thought to form from chill crystals which preferably grow in the opposite direction to the heat flow. Northcott (74, 75) has shown these crystals to be highly orientated to the growth direction as compared to the random orientation of the chill zone crystals. It is therefore thought that the columnar zone is formed by competitive growth amongst the chill crystals, those which are favourably orientated growing into the liquid in a dendritic manner and dominating the cast structure (73).

The central equiaxed zone in Fig. 3.15 consists of randomly orientated equiaxed crystals which grow in the melt ahead of the columnar crystals. The nucleation mechanism of these crystals is not known precisely although some theories have been proposed. The 'big bang' theory of Chalmers (66) proposes that when a mould is filled and chill crystals form at the mould wall, some of these crystals will not adhere to the wall but can be carried into the ingot centre by convection. Under the correct conditions these crystals will then form the nuclei of equiaxed grains.

The crystal shower mechanism of Southin (76) proposes that small crystals are formed on the upper surface of a solidifying ingot as shown in Fig. 3.16. These then sink due to the difference in density and grow before collecting at the bottom of the ingot to form the bottle shaped equiaxed zone often observed in large ingots.
A grain multiplication mechanism has been proposed by Jackson et al (77) who studied the solidification of metals using a transparent organic model substance which solidified between two glass slides on a light microscope stage. This material solidified in a dendritic manner. It was observed that the dendrites coarsened with time and that fluctuations in the growth rate could lead to the melting-off of dendritic arms due to local convection currents. These particles were then carried to the ingot centre and in this manner the transparent ingots were seen to form appreciable equiaxed zones by dendrite arm remelting.

The necessity for good convection in both the crystal shower and dendrite arm remelting mechanisms was demonstrated by Uhlmann et al (78) and Morndo et al (79) who solidified...
aluminium-copper alloys at various degrees of superheat under the influence of a strong magnetic field designed to counteract the normal sedimentation flow. They were able to inhibit the settling of equiaxed centre forming crystals and thus produce a fully columnar structure.

Fredriksen and Hillest (80) in their investigation of the columnar-equiaxed transition (C.E.T.) found that convection played an important role in the formation of an equiaxed structure by conveying growing crystals in the ingot's liquid centre to the solid columnar wall and thus effectively blocking further columnar growth. They also observed that a more jagged columnar solidification front could catch such floating crystals more efficiently than a smooth front and that during solidification of an ingot, the profile of a vertical solidification front changes from smooth to more jagged as a result of the decreasing thermal gradient.

Winegard and Chalmers (81) proposed that constitutional supercooling due to solute enrichment ahead of the growing columnar grains could explain the existence of the equiaxed zone, as discussed in the previous section. Tarshis et al (82) in their investigation of the cast grain size of aluminium and nickel upon addition of certain alloying elements were able to produce fine grain sizes when the value of a parameter, P, was greater than 10. This parameter was defined as

$$p = \frac{-m(1-k_0)c_0}{k_0}$$

where \(m\), \(k_0\) and \(c_0\) are as defined in the previous section.
This equation is almost identical to equation 3.24 giving the regime under which constitutional supercooling may occur, thus supporting the argument that this mechanism can contribute to the formation of an equiaxed structure. The observed results for nickel are shown in Fig. 3.17.

According to Engler (73) equiaxed grain forming mechanisms may operate simultaneously but they all require the formation of small crystals in the ingot centre which can then grow.

Fig. 3.17 Grain Size of Nickel as a formation of the parameter P. (82).
3.5 Grain Refinement

Grain refinement of a cast structure has been described by Turnbull et al (83) as involving a "reduction in length of the columnar grains, a refinement of the width of the columnar grains, a reduction of the size of the equiaxed grains, or a combination of any of these processes". On a finer scale, the refinement of the structure may also involve a refinement of the dendrites. Known methods of grain refining can be divided into three groups (24).

(1) Thermal Grain Refinement

It is well known that a fine equiaxed grain structure can be obtained by using a low pouring superheat of the order of 10K (60, 84, 1, 2, 76, 79). This is thought to ensure that any nuclei produced when the stream of molten metal contacts the cold mould wall survive and grow to form an equiaxed structure. Conversely, by employing high superheats a fully columnar structure may be encouraged. Although there are benefits associated with a fine structure, the pouring of melts with a low superheat is not a viable commercial proposition due to the associated problem of premature freezing resulting in incomplete filling of the mould.

(2) Stirring Grain Refinement

Much work has been undertaken to promote grain multiplication mechanisms by inducing convection currents to break-off dendritic areas within a solidifying casting which then pass into the liquid
where they can act as nuclei. Electromagnetic stirring (85, 86) as well as mechanical vibrating methods (87, 88, 89, 90) have been successfully employed to this end. The major disadvantages of this method are the cost of equipment and complexity of operation. However, the method is extremely controllable and has been used to produce single crystal turbine blades (good creep resistance) with fine equiaxed root sections (good fatigue resistance) (11).

(3) Constitutional Grain Refinement

Undoubtedly, the most commercially widely adopted method of grain refining is by making additions to the melt prior to casting and, in particular, making Ti and B additions to Al (91, 92, 93, 94). Such additions should be stable in the melt and produce particles which may act as heterogeneous nucleation sites. This requires the addition to be well wetted by the melt and it is proposed that there should exist a low lattice mis-match between certain planes of the nucleant and those of the bulk metal (94, 95). Methods of improving the dispersion of such grain refiners have been developed which include coating the mould surfaces with such inoculating powders (96), making additions of coated particles (1) or making powder additions as green compacts which dissolve in the melt (97).

Effective nucleants for Cu based alloys are reviewed and discussed below.
4. GRAIN REFINERS FOR COPPER AND COPPER BASED ALLOYS

The major problem when evaluating the literature on the subject of grain refinement of Cu based alloys is the consistent lack of accurate experimental procedures given in the text and the consequent apparent contradictions arising when comparing the results of different workers. Mannheim and Reif (98) list the various experimental parameters which can influence the grain refining additions to Cu based alloys (Table 4-1) and conclude that a comparative study of the literature is 'difficult to impossible'. The list, however, is not exhaustive and other authors have found it useful, for example, to record cooling curves of grain refining tests (99) or to attempt detailed microanalysis of suspected heterogeneous grain refining particles (100). These, however, depend on the use of modern techniques which were not available to early workers in the field (101, 102, 103). Therefore, bearing in mind the general lack of theoretical understanding of the processes influencing grain refinement and casting in general, the validity of the classical results must be open to question in many cases.

In the following, the effects of various additions to Cu and Cu based alloys will be discussed. Although this investigation is concerned exclusively with the refinement of brass alone, it would be a mistake to ignore the effects observed in other Cu alloys which may be applicable to this investigation.
1. Type & Constitution of Alloying Element.
2. Trace Elements (dependent on deoxidation means)
3. Deoxidation
4. Crucible Material
5. Dissolved or Rising Gases (e.g. - CO)
6. Grain Refining Addition and Method of Addition
7. Melting and Casting Atmosphere
8. Melt Cover Medium
9. Convection
10. Superheat and Casting Temperature
11. Holding Time
12. Cooling Rate (Influenced by Mould Temperature)
13. Frequency of Remelting

Table 4-1 Major Influences which should be taken into account when conducting Grain Refining Tests (98).

4.1 Pure Copper

By far the most detailed study of dilute Cu binary alloys is that of Backerud et al (99). They investigated the effects of cooling rate, composition and type of alloy system on the grain structure formed during solidification. The alloys were classified into seven systems depending upon the solidification reaction (eutectic, peritectic etc.) and the distribution coefficient \( k_0 \) of the elemental addition. From each of these systems only one dilute alloy was investigated giving little evidence that the particular alloy was representative of the system as a whole or that it is indeed justified to class dilute Cu alloys into these systems for
the purposes of grain refining tests. The seven systems are classified according to the phase diagrams of Hansen (115) and are given in Table 4-2.

Additions of 0.01, 0.05, 0.1, 0.5, 1.0 and 5.0 wt% element were made to melts which were allowed to cool either in the insulated or non-insulated crucible or in the furnace resulting in cooling rates of 0.25, 1.0 and 2.0 K/s respectively. Cooling curves were recorded and the specimens were cross-sectioned and etched to facilitate counting of the number of grains per square centimetre. The resultant grain densities were plotted on a log scale for outer grain density versus inner grain density as shown in Fig. 4-1. A well refined Cu specimen is represented, for example, by point A, the frequent initial nucleation leading to a fine outer structure around the circumference of the specimen and the frequent subsequent nucleation resulting in a fine equiaxed inner grain structure. Limited initial nucleation only represents the normal mould wall nucleation and growth, the alloying element having no significant effect on the final grain size.

Backerud (99) found that no elemental addition below 0.5 wt% produced a significant refining action; however, he observed two important grain refining mechanisms at the higher concentrations. The first concerning system 6 in Table 4.2 peritectic type reaction with a distribution coefficient greater than unity which was seen to have a marked refining
\[ m_0 = \text{outer grain density} \]
\[ m_i = \text{inner grain density} \]

Fig. 4.1 Nucleation mechanisms (a) and your representative structures (b) according to Backerud (99).
<table>
<thead>
<tr>
<th>SYSTEM</th>
<th>DESCRIPTION</th>
<th>DISTRIBUTION</th>
<th>EXAMPLES</th>
<th>INVESTIGATED ALLOY SYSTEM</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Complete solubility in both solid and liquid phases</td>
<td>$&gt;1$</td>
<td>Cu-Pd, Cu-Pt</td>
<td>Cu-Ni</td>
</tr>
<tr>
<td>2</td>
<td>Complete solubility in both solid and liquid phases with a minimum in the melting point</td>
<td>$&lt;1$</td>
<td>Cu-Au</td>
<td>Cu-Mn</td>
</tr>
<tr>
<td>3</td>
<td>Eutectic with high solubility in the solid phase</td>
<td>$&lt;1$</td>
<td>Cu-Zr, Cu-Cd, Cu-Mg, Cu-P, Cu-Ti</td>
<td>Cu-Ag</td>
</tr>
<tr>
<td>4</td>
<td>Eutectic with low solubility in the solid phase</td>
<td>$&lt;&lt;1$</td>
<td>Cu-B, Cu-Ca, Cu-Ge, Cu-Se, Cu-Te, Cu-La, Cu-La, Cu-Li</td>
<td>Cu-Bi</td>
</tr>
<tr>
<td>5</td>
<td>Peritectic</td>
<td>$&lt;1$</td>
<td>Cu-Al, Cu-Ge, Cu-Si, Cu-Sn, Cu-Ga</td>
<td>Cu-Zn</td>
</tr>
<tr>
<td>6</td>
<td>Peritectic</td>
<td>$&gt;1$</td>
<td>Cu-Fe</td>
<td>Cu-Co</td>
</tr>
<tr>
<td>7</td>
<td>Monotectic with low solubility in the solid phase</td>
<td>$&gt;&gt;1$</td>
<td>Cu-Tl, Cu-S, Cu-Se, Cu-Te</td>
<td>Cu-Pb</td>
</tr>
</tbody>
</table>

Table 4.2 The Seven Systems Investigated by Backerud et al (99)
effect above a specific concentration, a result confirmed by other workers (2, 102). The proposed mechanism in this case can be explained as:

\[
\text{Cu (liquid) + Co (solid) } \rightarrow \text{Cu (solid)} \quad 4.1
\]

Cobalt is precipitated from solution via the peritectic reaction where upon it acts as a heterogeneous nucleant for the Cu. Only in this case was an even grain refining action observed (i.e. such as would be represented by point A on Fig. 4.1) This was thought to be due to potent nucleating characteristics of the produced even suspension of solid Co in the liquid Cu. The proposed mechanism is supported by the cooling curve data (Fig. 4.2). Here Co additions are seen to require the smallest undercooling of the seven samples examined for solidification to proceed. This implies that there exists in such a casting a potent nucleant. Of particular interest is the fact that this refinement was observed at 1 wt% addition, well below the equilibrium concentration for the Cu-Co peritectic reaction to occur.

Gould et al (2) confirmed the effectiveness of Co additions below the 1 wt% addition level and investigated the effect of Fe additions to Cu melts, Fe being classified by Backerud as belonging in the same system as Co.
Fig. 4.2 Undercooling, \( \Delta T \), in the various systems as a function of composition. The most probable nucleation range, \( \Delta T^* \), is indicated. Below this the structure is mainly columnar and above it fine internal grains are expected as a result of copious nucleation.

Again, Fe was observed to have a grain refining action at 2.42 wt\%, below the equilibrium peritectic reaction.
concentration of 2.8 wt%. The resultant grain structure was fully equiaxed. Smaller additions of 1.32 and 0.02 wt% produced no refinement.

Patchett and Abbaschian (85) investigated the effect of high purity Fe on the cast grain size of pure copper and found the iron to have a small effect below the equilibrium concentration at which point a marked change was observed. The alloys were solidified either by water quenching (cooling rate 500°C/S) or while levitated in a strong magnetic field (abnormal stirring effects) so that there need not necessarily be any direct conflict with the previously mentioned results.

In the recent work of Trevisa and Cupini (104) 0.1 to 1 wt% of Fe and Co were added to pure Cu in the form of a salt, master alloy or powder in an attempt to activate the refining mechanism at lower additional concentrations. The results were consistent with those of Backerud (99) and Gould et al (2), no grain refining action was observed. It was further attempted to ascertain some information concerning the distribution of the added Fe after solidification using EPMA techniques. A relatively even distribution of Fe throughout the ingot as grain boundary particles was found, confirming the ineffectiveness of this mechanism at the lower concentrations.
The second mechanism observed by Backerud et al (99) concerns additions of systems 3, 4 and 7. In these cases limited initial and frequent subsequent nucleation was observed (Fig. 4-1.). The three alloying additions investigated: Bi, Ag and Pb were associated with a relatively large undercooling (Fig. 42), the extent of the grain refinement being directly associated with the amount of undercooling. These systems all involve elements with a distribution coefficient less than unity and Backerud proposed that the increased undercooling was due to a build-up of solute ahead of the growing columnar crystals which promoted the nucleation of new crystals in the central region.

Northcott (102) studied the effect of a large number of pure elemental additions, from 0.1 to 2.0 wt%, on a high round directionally solidified cast Cu ingot. The normal grain structure was fully columnar and Northcott measured every change in columnar grain length as a result of the refining addition. From this analysis an order factor was established called the 'Growth Restricting Factor' (GRF). The lower in the order were the poorer grain regions and the higher order values had a marked effect upon the crystal size. However, whereas Backerud quoted elements of the eutectic system with a low distribution coefficient as being potent refiners, Northcott found that they had very little effect on the columnar grain size. Bismuth is assigned a GRF of 1, indicating that of the 35 elements investigated, bismuth had the least effect on the crystal structure. Of
the same system (from Backerud) Li has a GRF of 11, Ca 20 and B 23. The strongest growth restrictions were found to occur in Backerud's series 7, Pb achieving the most marked effect with a GRF of 35, Tl of 34 and Se of 30. Thus, Northcott made similar additions to Backerud but found very different results. The reasons for this must lie with the experimental method, about which Northcott gives very little information. For example, no reference is made to the purity of the Cu; means of deoxidation; holding time; holding atmosphere; casting temperature and the method by which the additions were made. The casting technique used by Northcott was the Durville process where a holding crucible is positioned under an upside-down mould, the crucible is filled with molten metal and when casting is to proceed the whole device is inverted. One can foresee the situation occurring where low purity Cu is melted without deoxidation and oxidisable grain refining additions (Li, B, Ca) serve only to deoxidise the melt; any unreacted addition rapidly being removed from the melt as the molten Cu absorbs oxygen from the atmosphere. This therefore could resolve the apparent conflict between the results since many of the elements having the worst GRF properties are those which are highly reactive with oxygen (e.g. Al, Li) and vice-versa (e.g. Pb, Pt, O). Indeed, if oxygen is a good grain refiner (GRF = 32) any addition which removes it should have a negative grain refining effect.
Backerud's results are, however, corroborated by Gould et al (2) who found the effects of Li and Bi on chill cast Cu were to promote a highly equiaxed fine grained central region in the ingot. This type of addition is quoted by the authors as having a strong constitutional supercooling function and it was therefore found that two or more such additions could be used in the same melt to increase the refining action.

Tuttle (105) investigated the effect of growth restricting additions to pure Cu as predicted by the Tarshis parameter P (described in Section 3.4). Tarshis and his co-workers (82) in their work on Cu Ni alloys and Al found that when the value of this parameter P (given in equation 3.26) was above a critical value (about 10) a considerable grain refinement occurred. Tuttle (105), however, found no correlation between this parameter and the final grain size despite testing over 15 elements at addition concentrations of 0.5 and 1.0 wt%. Many elements of high P value are quoted by Backerud (99) as having good grain refining properties (e.g. Bi, Li). This is not surprising since Backerud based much of his work on the value of the solute distribution coefficient which also is one of the major parameters in the Tarshis equation defining P. Tuttle failed to measure or control his pouring temperatures which may explain the inconsistent results he found, especially amongst his more detailed investigation of the influence of titanium, boron and tellurium.
Jones and Weston (106) and Southin and Weston (107, 108) used a technique to flux out heterogeneous nuclei from the Cu melt prior to final freezing whereby the melt was continuously frozen and remelted in a silicon crucible under a soda glass cover. The measured undercoolings increased with the number of remelts after a maximum of 200K. In this manner they were able to study cast Cu microstructures solidified at a precise undercooling. Initial results (106) showed that the cast grain size of pure (99.999%) Cu was independent of the undercooling. However, small additions (0.015 wt%) of oxygen produced a well refined structure at undercoolings of between 22 and 59K. Smaller undercoolings resulted in a mixed fine columnar-fine equiaxed structure, whereas larger undercoolings resulted in a fully columnar structure. These results were explained in terms of a solute rejection mechanism whereby the growing secondary dendrite arms have to grow through a lower melting point oxygen enriched layer. Recalescence and back diffusion of heat down the secondary arms could cause melting of the necks of the secondary arm branches. Subsequent fragmentation and convection would lead to the presence of many nucleating species within the melt. The above mechanism is not operative at higher undercoolings since recalescence does not provide enough heat to remelt the secondary dendrite arms. This work was later repeated (107, 108) with additions of S and P instead of oxygen. Similar results were recorded. However, it was found that larger additions of S at higher undercoolings also resulted in grain refinement for which the authors offer no
satisfactory explanation. Grain refinement, however, could be due to the initial precipitation of a sulphide particle.

In a patent application Van Achter (109) details a method for grain refining Cu by the addition of 'growth inhibiting components' to the melt. These components consist of 0.01-0.1 wt% B, 0.1 - 1.0 wt% Zr and/or Ti combined with/or not 0.1 - 1.0 wt% Al. A preferred composition is quoted as 0.4 wt% Al and 0.02 wt% B which results in an as cast grain size of 120um (no other casting details were given). A grain boundary network was identified and microprobe analysis proved this to be rich in both B and Al. Some angular precipitates are also observed within the grains but no further details of these were given. It is further stated in the patent application that this grain boundary network also inhibits grain growth after cold working and high temperature annealing, thus producing a material not susceptible to the 'orange peel' effect.

Reif and Weber (110) in another patent application give grain refining additions which, it is claimed, are suitable for refining all Cu based alloys. 0.01 - 0.1 wt% Zr or Ti is added to the metal along with 0.01 - 0.1 wt% of any element in group one in Table 4-3, 0.03 - 0.1 wt% of any element in group 2 and 0.003 to 0.02 wt% of any element in group 3, the original Ti or Zr addition not being repeated. The inventors' claim to have listed all but a few of the rarer additions and to have achieved consistently good results.
Group 1  
Li  Be
Na  Mg
K  Ca
Sr  Ba

Group 2  
Sc  Ti  V  Cr
Mn  Fe  Co  Ni
Cu  Zn  Y  Zr
Nb  Mo  Tc  Ru
Rh  Pd  Ag  Cd
Hf  Ta  W  Re
Os Ir  Pt  Au

Group 3  
Al  Si
P  S
Ga  Ge
As  Se
In  Sn
Sb  Te
Tl  Pb
Bi  Po

Table 4.3 Grain refining additions for Cu based alloys according to Reif and Weber. (110)

4.2 Brass

As reported by Backerud (99), Zn has little effect on the as cast grain size of Cu. Northcott (103) measured the columnar grain size of Cu-Zn alloys cast into chill moulds and directionally solidified (Fig. 4-3). The addition of Zn results in the crystals becoming only slightly less columnar than those of pure Cu and even towards the limit of the alpha solid solution the crystal length was only reduced by a half. Upon precipitation of the primary beta phase the crystal length increased again so that most of the alpha-beta and beta brasses solidified with a fully columnar structure.

De Galiza and Cupini (111) investigated the effect of Fe on commercially pure alpha brass. They observed little reduction in grain size at concentrations up to 0.85 wt% and a drastic reduction at levels of 1 wt% and more.
Fig. 4.3. Variation in columnar crystal length with composition as found by Northcott (103)

- Cast with 120K superheat
- Cast with 150K superheat

This was attributed to a peritectic reaction, as described earlier, whereby pure Fe is precipitated from the melt and acts as a heterogeneous nucleant. The amount of superheat was seen to have no effect once inoculation had taken place. The Fe peritectic concentration in brass is considerably lower than that in pure Cu. French (17) points out that this peritectic concentration (1 wt%) of iron in the alpha phase is about the same as that in the beta phase and that this mechanism is just as effective in beta brasses. The value of 1 wt% in alpha alloys is also supported by Oga and Toda (3) who undertook similar experiments and by Davies and Lloyd
(5) who tested complex Al and Si containing two phase brass and found that the quantity of Fe necessary to achieve refinement decreased as the Si content increased.

Cibula (101) states that almost all fully beta commercial brass castings are normally fine grained due to their high Fe content. He further states that there are cases where Fe free alloys are required (presumably for machining). He therefore cast 33 wt% Zn, 4 wt% Al containing B alloys at 1340°C making additions of Zr and B. Each element was seen to have only a small effect on the grain size but 0.06 wt% Zr with 0.024 wt% B resulted in a grain size of 0.7mm in 50mm chill cast B. It was assumed that zirconium diboride particles were formed which acted as potent nucleants. No direct evidence of this occurring is given.

Weber (112) studied the refinement of leaded duplex brass with 0.002 wt% B added as Cu - 2 B masteralloy to a 500kg melt. He found pre-deoxidation with Cu-Mn to be necessary in order to ensure consistent results showing a fine equiaxed grain structure (not quoted but estimated at about 300mm grain size) and improved casting and mechanical properties. Without deoxidant added he assumed that the B addition acted as a deoxidant. Doubling the amount of B only served to worsen some of the casting properties and the lower addition level was considered optimum.
Boron was also employed by Davies and Lloyd (113) to reduce a fully columnar duplex high tensile brass (containing 1.5 wt% Al and 0.5 wt% Mn) to an equiaxed structure with a 0.8mm grain size. The grain size could be further reduced to 0.5mm upon addition of 1.3 wt% Fe. However, grey-purple particles were then observed to agglomerate after remelting and freezing. These were subsequently analysed and found to contain Fe, Mn and B.

Elst and co-workers (115) grain refined Cu-Zn-Al and Cu-Al-Ni shape memory alloys with separate additions of Co, Ti and B. Ti additions of up to 1 wt% were seen to transform the columnar and equiaxed structure (equiaxed grain size 1-5 mm) to fully equiaxed some 150-250 um in diameter. A 0.4 wt% addition of Co to the Cu-Zn-Al alloy was seen to have no effect at all. A 0.04 wt% addition of B to the Cu-Al-Ni alloy had no significant effect while a 0.1-0.2 wt% addition greatly reduced the grain size to 50-100 mm. A 0.04-0.06 wt% addition of B to the Cu-Zn-Al alloy gave a very fine 50-100 mm grain size while larger or smaller additions gave poorer results. Thus, in both alloys B was seen to provide the greatest refining action. Unfortunately, the precise composition of the Cu-Zn-Al alloy is not given. In a later publication (116) the authors' describe a shape memory alloy of composition Cu 73.6 - Zn 20.2 - Al 6.2 wt%. It is proposed that the B forms AlB$_2$ or AlB$_{12}$ particles which act as potent nucleants in the melt. Second phase particles were seen in the alpha regions of the two phase alloy but no
analyses of these is given despite claims to have employed WEDX analysis (see chapter 5). By considerations of the volume fraction the authors find that the particles "might be of the AlB$_2$-type" but are unable to satisfactorily explain how they can grain refine a beta solidifying alloy when they are seen to nucleate the alpha phase. No detailed microstructural investigation of the refined alloy is made and no grain refining mechanism is investigated.

The work of Reif and Weber (110), described in the previous section, has been applied to alpha brasses and a recent publication (100) reports the successful refinement of alpha, dezincification resistant alpha and leaded alpha brasses. Reif and Weber report the presence of many fine particles in such brasses refined with Zr, Mg, Fe and P according to application. These were claimed to be heterogeneous nuclei and were analysed by X-Ray wavelength dispersive technique. They were found to contain the four added elements plus oxygen and sulphur. Subsequent electron diffraction studies showed that there is a relatively large mis-match between the lattice parameter of the matrix and that of the particles. The authors suggested that the particles are active nucleating centres.

Cowell and Nixon (18) have further investigated the claims of Reif and Weber (110). They successfully grain refined alpha brass using Zr and Mg and reported that Mg alone had no significant effect although Zr alone was partially successful
and its effect was increased when Mg was present. They propose that the Mg oxidises preferentially, protecting the Zr in the melt, the free energy of formation of Mg oxide being slightly lower than that of Zr dioxide at the appropriate temperatures. This implies that the Zr is the most important grain refining addition.

In this respect it is interesting to note the work of Yarwood (114) who added 0.002 - 0.5 wt% of P and 0.002 - 1.0 wt% of a transition metal to a 70 - 30 brass cast at 1020°C. The transition metal was selected from Zr, La, Ti, V and Mn mixtures thereof. The only example given shows a fine grained casting refined with 0.1 wt% P and 0.5 wt% Zr. Since P is a standard well known deoxidant for Cu-based alloys it could be expected that the Zr may be protected from oxidation much in the same manner as proposed by Cowell and Nixon (18).

4.3 Tin Bronzes and Gunmetal

The effect of the addition of Sn and lead to copper has been studied by Northcott (103) who measured the length of chill cast columnar crystals after the addition of the alloying elements. 0.5 wt% Sn was seen to reduce the original three inch crystals to 12 mm. Increasing the quantity of Sn rapidly increased the crystal length so that at 4 wt% 50 mm long columnar grains were apparent, this length increasing only slightly as the Sn content was increased to over 30 wt%. The addition of Pb to Cu greatly decreased the crystal size
even at small concentrations, in agreement with the observations of Backerud (99) and the effect of Zn already discussed in the previous section. Thus, it may be expected that leaded bronzes would be naturally fine grained due to the action of the Pb. This has been confirmed by Coulton and Mongolis (16) who added the alloying constituents of an 85-5-5-5 separately and in various combinations to Cu and found a marked reduction in grain size only when the Pb had been added.

Cibula (101) carried out extensive grain refining tests on sand cast Cu - 10 wt% Sn alloy. He found that Mg (up to 1 wt%), Ni (up to 2 wt%) and Cr (up to 1 wt%) produced no significant grain refinement while Zr and Ti greatly reduced the grain size. The most marked effect was produced by 0.02 - 0.03 wt% Zr if C was in contact with the melt (crucible constituent, graphite cover, etc.). Cibula assumed that this was due to the formation of a carbide in the melt which would not happen under "continuously oxidising conditions which would eliminate carbon". Considering the hypothesis of Cowell and Nixon (18) a better explanation may be that Zr is oxidised under "continuously oxidising conditions" and that the C itself only serves to protect the Zr from the oxygen. Cibula (101) produces no evidence to support his claim that Ti or Zr carbide is produced. The addition of S to a Zr and C inoculated melt was seen to destroy the refining action, supposedly due to the preferential formation of Zr or titanium sulphide. The refining action was
restored in such circumstances if Mn additions were made. Manganese was presumed to react with the S to form MnS.

Cibula (101) also found Fe at concentrations above 1.6 wt% to grain refine Cu 10 wt% Sn alloy. This is to be expected from Backerud's work (99), since the alloy is based upon the alpha Cu solid solution. He also observed the onset of formation of primary Fe rich dendrites at this concentration and assumed that they were responsible for the refining action. Mannheim and Reif (98) repeated some of Cibula's work successfully refining Cu 4 wt% Sn alloy with 0.06 wt% Zr and 8 wt% Sn alloy with 0.02 wt% Zr. The refining action improved when the melt contained also 0.02 wt% P (Fig. 4.4). It should be again noted that the phosphorous acts as a deoxidant in commercial practice. The authors found B to increase the grain size of Sn bronzes (Fig. 4.5).

Fig. 4.4 Dependence of Average Grain Diameter on the phosphorus concentration of a Cu Sn 4 alloy with 0.06 we % Zr (98)
Fig. 4.5 Dependence of Average Grain Diameter and Brinell hardness of Cu Sn4 and Cu Sn8 Alloys with and without additions of Zr and B on the Holding Time. (98)

Breme (127, 118) in his investigation of the influence of the grain size on the mechanical properties of Cu 15 wt% Sn alloys grain refined successfully the cast alloy with Calcium hexaboride. No details of the casting conditions or the quantities of addition were given. A well refined structure was observed with an estimated grain size of 250mm.

4.4 Aluminium Bronzes

The effect on the cast grain size of adding up to 15 wt% Al to Cu has been investigated by Northcott (103). He found that when chill cast at constant superheat, the columnar crystal length could be correlated fairly closely with the equilibrium phase diagram in so far that the maximum length was obtained when the freezing range was smallest (Fig. 4-6).
Detailed investigations into the grain refinement of Cu 10 wt% Al alloy are described by Dennison and Tull (119). Uncertain as to whether this alloy would solidify with alpha or beta as the primary phase the authors tested additions suitable for both as given by consideration of the lattice mis-match. Small ingots were poured at a constant rate and a temperature of 1423K. Under such conditions the untreated castings had a fully columnar structure. Of the innoculants thought suitable for nucleation of the alpha phase, the particles of Ca, Ce, Co, Ti and Zr all produced marked

Fig.4.6 Variation in columnar crystal length with composition as found by Northcott. (103)

- Cast at 1473K
- Cast with superheat of 100K.
- Cast at Intermediate temperature.
grain refinement, the columnar grains being replaced by a fully equiaxed structure with an average grain diameter of 0.5 mm. Tetraboron carbide, presumed to be a beta nucleant, produced by adding Cu-B master alloy prior to bubbling acetylene through the melt, was also seen to produce a similar equiaxed structure. Dennison and Tull then made additions of B alone to Cu containing 7.5, 10.0 and 12.5 wt% Al representing the all alpha, duplex Alpha Beta and all beta microstructures. This was done in order to investigate whether B produced the refining action either by itself or in conjunction with something else already present in the melt. They found that B refined successfully the alpha beta and fully beta alloys. It was suggested that the degree of refinement could be increased as the amount of B added was raised from 0.0025 to 0.03 wt%. The refinement produced by these B additions was seen to be unaffected by repeated remelting and casting but the duplex alloy did show a deterioration of the effect when the lower additions were cast at a higher superheat. The authors proposed the nucleating species active in this refinement to be tetraboran carbide. No evidence is presented to support this claim.

Later work by the same authors (120) was directed at the all alpha alloy containing 7-9 wt% Al. They found about 0.1 wt% of Mo, V, Nb or W to reduce the columnar grain size slightly but the borides of these metals or B itself had no effect on the alloy containing less than 8.25 wt% Al. Above this value an addition of 0.02 wt% B was very effective. Since
it was expected that the alpha phase would be the first phase to precipitate from the liquid and considering their earlier work which showed that the alpha phase was not required by B in the way that the beta phase was, they hypothesised that the undercooling produced under their experimental conditions was sufficient for the beta phase to be nucleated by extrapolation of the beta phase liquidus below and beyond the eutectic point. When the Al content was reduced from 8.25 to 8.24 wt%, the refining action did not occur implying that in this case the alpha phase was precipitated which was not refined by the undercooling species.

Dennison and Tull (119) tested many transition metal carbides and borides as grain refiners for the alpha alloy but without success. Breme (117, 118), however, reports that Ca hexaboride can be used to grain refine Cu - 8 wt% Al alloy. No details of the casting conditions, final grain size or precise analysis of the alloy were given.

More recent work on the refining of Al bronzes with B has been published by Rodolfo, Mannheim et al (122) and Mannheim and Reif (98). They found that a Cu 6 wt% Al alloy could be refined by B only if C was also present in the melt. The optimum addition is reported as 0.01 weight percent B and 0.045 wt% C for a melt cast at 1350 - 1450K into Fe moulds. This gave a grain size of between 150 and 200 mm. No refining action was observed in the absence of the C, an observation similar to that of Dennison and Tull in the beta
alloys (119). Mannheim and Reif (98) then undertook microstructural investigation of the refined alloy and found particles rich in Al and B and O$_2$ by using a wavelength dispersive analysis technique in the SEM. They propose that such a mixed compound acts as the nucleant. No definite range of composition or details of how many such particles were investigated were given.

The effect of addition of Fe and Co, which were found to be so effective on many alpha Cu alloys, was investigated on beta alloys by Feest (123) and Hasan et al (124). Neither worker reports any significant effect but Hasan et al (124) describe the precipitation of many fine Fe rich particles of the alpha phase by heterogeneous nucleation as the alloy cools. Thus, the Fe acts as a nucleant for alpha precipitated from solid solution and not for the initial beta precipitated from the liquid.

4.5 Summary

Despite the difficulty in comparing the results of different workers, there is considerable evidence to support the following:

(i) The peritectic reaction is effective in grain refining copper based alloys. Cobalt and iron grain refine the alpha alloys by this mechanism.

(ii) Elemental additions having a very low distribution coefficient have been observed to grain refine copper based melts.
(iii) Zirconium is an effective grain refiner for alpha brass and bronzes if protected from oxidation in the melt.

(iv) Boron is an effective grain refiner for beta brass and aluminium bronzes.
5. Experimental Work

5.1 Introduction

Grain refinement of a two phase brass using an Al-4B master alloy was first observed by Cowell and co-workers (125). The refined ingot is compared to the normal structure in Fig. 5.1. (both cast at Surrey). Three distinct zones are apparent in the refined ingot (fig. 5.1a) as compared to the two zones (fine chill crystals and columnar grains) in the control ingot (fig. 5.1b). The first outer zone of fine chill crystals is similar to those found in the untreated ingot but in all other respects the grain structure is markedly different. A central area of very fine equiaxed crystals can be seen which is separated from the fine outer chill crystals by a thick layer of coarse equiaxed crystals (fig. 5.1a). It should be noted that there exists a very clear delineation between the coarse and fine equiaxed areas with no coarse crystals present in the fine area and vice-versa. The delineation between the chill and coarse equiaxed is much more gradual than the sharp interface of coarse to fine equiaxed which is shown in greater detail in Fig. 5.2. The Widmanstaetten precipitation of the alpha phase normally associated with a cast brass of this composition can be observed in both coarse and fine areas. This describes the basic refining effect observed and the conditions necessary to achieve this effect are given below.
Fig. 5.1 Grain refined brass (a) and non-grain refined brass (b) in cross section and refined in longitudinal section (c).
5.2 Melting and Casting Practice

The standard practice was to melt a weighted amount of scrap electrical copper in a salamander crucible. Scrap electrical copper was used as this was of high purity. The metal was cleaned as necessary to remove any sources of contamination. The copper was then melted in air. No degassing addition was made. The temperature was measured using disposable Land Pyrometer thermocouple lances and at

Fig. 5.2 Optical micrograph of the coarse-fine equiaxed boundary in the refined brass. Etch: acidic ferric chloride solution.
about 100K superheat the required amount of zinc was added. It was this stage that determined the minimum practical melt size since in order to avoid successive loss of Zn through air oxidation, the Zn metal had to be held under the surface of the Cu until it had dissolved. If the crucible contained too little copper the zinc would fume and burn at the copper surface. An Ar shroud could be placed over the surface but it was found to have more of a stirring effect drawing fresh air to the Cu surface. To avoid introducing moisture to the melt the Zn was pre-heated to some 150K above room temperature. The melt superheat of 100K prior to the addition of Zn was found to be necessary due to the bulk cooling effect of the cold metal. Although Zn lowers the liquidus of the Cu melt (see Fig. 5.3) this does not offset the overall cooling effect when a superheat of 100K was not used the crucible contents became 'pasty' or solid.

The melt was left some 15 minutes for any temperature fluctuations to come to an equilibrium. One problem associated with the melting of brasses is the high vapour pressure of Zn in the melt which leads to excessive zinc loss if the melt temperature rises much above about 1050°C. The amount of Zn lost to the atmosphere could be kept to a minimum by careful temperature control and use of a standard crucible cover. It has been proposed that the effect of Zn evolution is to produce a self deoxidising melt (126). However, Weber (127) showed that such melts still contained considerable amounts of dissolved oxygen.
Fig. 5.3 The Cu-Zn Phase Diagram
Refining additions were added according to their form either by plunging and holding under the surface until they had dissolved (bulk solids) or following encapsulation in copper foil these were held under the melt surface (particulate matter). The additions were again thoroughly dried before being added to the melt.

The standard mould used in this investigation produced specimens measuring 38mm in diameter by 100mm in length and was made from a drilled section of scrap graphite electrode 160mm in diameter by 190mm in length. A graphite mould is classed as a chill mould having a relatively large thermal conductivity coefficient of 47W/m/K at 1573K compared to the value of 1W/m/K at 1373K for a sand mould (116). After casting the melt surface became solid after 10 seconds and after a minimum of 120s the pencil ingot was removed by inverting the mould. The moulds were always slightly pre-heated (by about 50K) to drive off any moisture prior to casting and were always allowed to thoroughly cool again before being re-used so that no mould pre-heat was accidentally used. Any molten metal not used was cast into an iron mould and scrapped. The empty crucible was then thoroughly cleaned while hot by scraping the walls and bottom.

Control specimens were cast before any refining additions were made to ensure that any refining action observed was not due to any unintentional actions. The temperature and time
of casting and temperature of the melt was recorded and the cooled specimens were stamped for identification.

A summary of the standard casting practice employed in this work and also in the work of Cowell (125) is given in Table 5.1. The only difference with the casting practice of Cowell is the type of furnace used by him, a relatively slow heat-up resistance furnace, whereas in this work faster heat-up rate induction furnaces were employed with an associated better stirring effect. This difference was not seen to have any obvious effect on the observed grain refinement.

Raw Materials
- Scrap electrical grade Cu
- Scrap commercial purity Zn
- Commercial Al-4B master alloy

Melting
- Induction heating of salamander crucible
- Air atmosphere
- No deoxidation no cover
- Cu melted, Zn added at 100K Superheat
- Addition made

Casting
- Into graphite moulds
- 100K superheat

Table 5-1 Standard Casting Conditions

5.3 Microscopical Examination of the Grain Refined Structure

In the past many of the now common analysis techniques (e.g. EPMA, XRD and X-Ray diffraction) were not available and researchers could not be sure as to which reactions had taken place in a liquid melt when various additions were made in a grain refining experiment (101, 102, 119, 120). Modern
practice is to try to determine exactly the composition of any centre of grain refining activity. Backerud et al (99) used dispersive X-Ray microprobe analysis to qualitatively determine the composition of Fe rich particles found in Fe inoculated copper. Their results are only qualitative since the Fe rich particles were analysed after polishing the Cu specimen. Thus a large background count from the Cu matrix could be expected in this analysis. Reif and his co-workers (5, 98, 100) have used both wavelength dispersive microprobe and X-Ray diffraction to get chemical and structural information about possible grain refining particles in Cu based alloy specimens. Tuttle (105), however, in his Ph.D thesis entitled "Investigation into the Grain Refinement of Copper", made various additions to copper melts without undertaking a single microstructural investigation. Indeed, Tuttle (105) fails to present any refined micrographs at all preferring to rely upon grain size measurements and cooling curve information.

Investigation of the cast microstructure formed the starting point of the experimental work in this project. Initial sectioning, polishing to micro-diamond paste finish and etching in acidic ferric chloride solution revealed the microstructure shown in Fig. 5.1 (a) to (c). No other structural features were revealed by this standard technique. However, when the specimens were polished for an extended length of time a number of distinct 'hard spots' were revealed as shown in Fig. 5.4.
5.3.1 The Electropolishing Technique

To permit a more detailed study of these features the specimens were electropolished. This required soldering a contact wire to the back of the specimen prior to it being embedded in a cold set mount as shown in Fig. 5.5. The 40% aqueous ortho-phosphoric acid electrolyte was held between 325K and 340K for polishing and was replaced when it acquired a faint blue colour. Best results were always achieved using fresh electolyte. A potential difference of 2.2V was applied for 30 seconds to a specimen polished to a 6 mm diamond paste finish. The specimen was then quickly washed with distilled water and replaced in the electrolyte for a further 30 seconds polishing. This two stage electropolish removed any dirt present from the mechanical polishing in the first electropolishing layer by the intermediate wash and in general resulted in an enhanced, smoother finish. The potential difference source used was a Hewlett and Packard 6281A DC power supply.

The fine equiaxed grain area from the centre of the grain refined specimens is shown in the optical micrograph Fig. 5.6. The preferential dissolution of one of the major phases present gives considerable relief contrast which could be viewed better in the SEM which offers
Fig. 5.4 SEM Micrograph of Over Mechanically Polished Surface of a Grain-Refined Brass showing the presence of hard particles.

Fig. 5.5 Specimen Mounted for Electropolishing
greater depth or field, Fig. 5.7. The electropolishing technique revealed a phase which was not previously observed using optical techniques, namely a feathery lightly contrasted phase. Microprobe analysis was used to identify the two brass phases. The solidification sequence was as that expected for the 60-40 composition brass from the equilibrium phase diagram (Fig. 5.3). The brass initially solidified with a fully beta structure and as the alloy cooled the alpha precipitated later at the original beta grain boundaries. Fig. 5.7 shows islands of beta surrounded by the alpha phase. The feathery precipitate can thus be assumed to outline the original beta grain boundaries. Occasionally spherical particles were found near or in the feathery phase of a size consistent with the size of the hard particles shown in Fig. 5.4.

Fig. 5.6. Optical Micrograph of the Electropolished Grain-Refined Brass
5.3.2 Microanalysis of the Grain-Refined Structure

Initial attempts to gain chemical analytical information about the feathery phase using both energy dispersive X-Ray analysis (EDX) and windowless energy dispersive X-Ray analysis (WEPX) in the microprobe proved inconsistent and difficult due to the small size of the precipitate. EDX analysis did provide evidence for the presence of aluminium in this feathery phase but WEDX analysis for light elements did not record the presence of boron. It was felt that the microprobe technique was too inaccurate and insensitive for this type of investigation and the microprobe was used only
to analyse Zn, Al and Cu concentrations in the bulk specimens.

Since addition of B to the melt was essential to produce a grain refined structure it was decided at this stage to employ more advanced techniques. The techniques initially considered included Secondary Ion Mass Spectroscopy (SIMS), Laser Induced Mass Analysis (LIMA) and Auger Spectroscopy.

SIMS' investigation was undertaken on an electropolished grain refined specimen as shown in Fig. 5.8 (a). This image was produced by a secondary electron detector and illustrates one of the major disadvantages of this technique (comparing Fig. 5.7 (a) to Fig. 5.8, the conventional SEM image of the same material). Fig. 5.8 (b) shows a boron map of the same area as in the secondary electron image. Although boron has been detected and areas of boron concentration have been found within the sample, it is very difficult to associate the boron with any particular feature within the specimen.

The LIMA facilities at Cambridge University were used but again the problems of imaging and definition of the very fine precipitates requiring analysis were encountered. In the LIMA method a plasma of ions formed by a focused high power laser beam pulse is analysed. Unfortunately, the focusing of the laser relies upon a low powered (X100) light
Fig. 5.8 (a)  SIMS' Secondary electron image of electropolished grain-refined brass.

Fig. 5.8 (b)  SIMS' boron map of specimen in Fig. 5.8 (a).
microscope and cross-wire mechanism. The fine nature of the precipitates requiring analysis made it impossible to confirm what was being targeted by the laser although a definite boron peak was recorded on several occasions as shown in Fig. 5.9 (a) which was not observed in the brass matrix Fig. 5.9 (b). Because of the problems of focusing on the fine precipitates the LIMA technique was abandoned although other workers have used LIMA to analyse for B in a melt spun Cu-2 wt% B ribbon on a comparative basis with some success (130).

The electropolished specimens were loaded into the Auger electron microanalyser. The feathery precipitates were clearly observable at the 10kV accelerating voltage used. A spot analysis of the precipitate was successfully undertaken and the resulting spectrum is shown in Fig. 5.10. A clear boron peak is seen along with carbon, oxygen and sulphur as well as a much smaller silicon peak (the carbon peak was expected since the specimens were in the form of extraction replicas on a carbon film as described below). This technique proved the feathery feature boron rich. However, due to the considerable difficulties in quantifying the results requiring comparison of acquired spectra with those from standard sources and the successful development of a fourth technique (described below) offering much greater resolution, the Auger analysis method was not pursued any further.
Fig. 5.9 (a) LIMA analysis of a feature found in the electropolished grain-refined brass.
Fig. 5.9 (b) LIMA analysis of the electropolished brass matrix.
Fig. 5.10 Auger analysis of the feathery precipitate in the grain refined brass.
Transmission Electron Microscopy (TEM) with its high resolution images is well suited to the investigation of the fine feathery grain boundary phase. The feathery phase was removed from the electropolished brass surface using a standard extraction replication technique (131, 132, 133, 134) see Fig. 5.11. The extraction replicas of the feathery phase were supported on a thin carbon film on a small round copper grid. This grid could be placed in the column of a TEM using a standard specimen holder to facilitate observation and analysis of the extracted features. It was found that better results were achieved by electropolishing the specimen for a second longer period (90 seconds) which left more of the precipitate standing proud of the surface. Typical examples of extraction replicas are shown in Fig. 5.12 (a) to (d) and in these micrographs the highly branched shape of the precipitate is clear. These branches often appeared to radiate from a round nodular centre about 2 mm in diameter. In all feathery structures observed in the TEM no significant difference in shape or size of the branch diameter was noted. The carbon film was often noticed to be contaminated with the acetate in parts, the dissolution of the acetate replicating sheet by the acetone being incomplete. However, too violent washing destroyed the carbon film altogether and cracks were often found in the film as apparent in Fig. 5.12.
(a) Electropolished brass.

(b) Layer of cellulose acetate softened with acetone on surface and left to harden.

(c) Cellulose acetate stripped off.

(d) Acetate coated with carbon.

(e) Acetate dissolved away while carbon film supported on TEM grid.

Fig. 5.11 Preparation of extraction replicas.
Fig. 5.12 (a) - (d) Various Examples of Extraction Replicas taken from the Grain Refined Brass. Further details of specimens are given in Appendix.
One completely unexpected property of the feathery type phase was its repeated failure to give any diffraction spot pattern diffraction. Instead diffuse ring patterns were recorded under selected area diffraction conditions, such as shown in Fig. 5.13 implying that the material was amorphous or glassy. These diffuse rings were seen to appear and disappear as the diffraction spot was traced over the feathery precipitate and was therefore not due to the carbon film.

Chemical analysis of the glass was undertaken using windowless X-Ray energy dispersive (WEDX) techniques and electron energy loss spectroscopy (EELS) in a Philips EM400T transmission electron microscope. The use of EELS for elemental analysis is best suited to the analysis of low atomic number elements which give sharp K-or L-edges in lower loss spectra, for example the K edge of boron, in Fig. 5.14 (a). The technique and quantification of the resultant spectra have been reviewed elsewhere (135, 136). Initial EELS spectra were collected from extraction replicas made from the grain refined brass with a nominal 60/40 copper/zinc composition and an addition of 0.8 wt% Al-4B master alloy. A typical EELS spectrum collected is shown in Fig. 5.17. No carbon K edge is observed here since the glass in this instance lay over a crack in the film. The oxygen edge becomes more apparent by expanding the vertical scale in that region Fig. 5.11(b) and can be ratioed to the boron content by comparing the areas under the peaks once a background stripping function has been applied. The major problems
associated with obtaining good spectra were the necessity to find thin sections and the observed low oxygen concentrations. EELS spectra of thick sections, giving a low boron concentration, could be easily recognised by the presence of several "plasmon" peaks at the lower end of the energy spectrum (compare Fig. 5.15 and 5.14 (a)) as reported in the standard works on the subject (135). Boron to oxygen atomic ratios of between 16:1 and 40:1 were calculated for individual spectra giving an average B:O ratio of just over

Fig. 5.13  The ring diffusion pattern associated with the feathery precipitate.
20:1 with a standard deviation of 8.6. Considering the accuracy of the EELS technique which is often quoted as ± 30% and the small size of the oxygen peak this relatively large standard deviation is not extreme.

At this stage it was decided to check the results of the EELS technique using powdered diboron trioxide glass on a carbon film. This was considered important since diboron trioxide is a well known glass. Thus it was necessary to establish whether the observed glass was a diboron trioxide/glass or a glass based on amorphous boron. In the analysis of the powdered glass a much larger oxygen peak was detected and three separate spectra gave results to within a few percent (well within the limit of ± 30%) of what would be expected. Thus, it became clear that the glass was not based diboron trioxide.

Windowless energy dispersive spectroscopy (WEDX) was used to ratio the concentrations of all other elements present in the glass to the oxygen concentration. All analyses were undertaken using a LINK Systems LZ-5 detector with a turret carrying a conventional beryllium window and a hole for windowless analysis. The detector was mounted at an elevation of 70° above the specimen position and analyses was carried out at 100kV potential with the sample tilted 30° towards the detector. A typical spectrum is shown in the upper trace of Fig. 5.16. The carbon from the support film gives a distinct peak. This is absent from the lower trace in Fig. 5.16 where the analysis was taken from the feathery.
phase overhanging the support film such as in Fig. 5.12 (c) and the boron peak becomes evident. This problem of boron and carbon peaks overlapping in WEDX has been encountered by other workers (137,138,139) with conflicting success and failure.

Fig. 5.14 (a) An EELS spectrum of the glass showing a sharp boron K edge.
Fig. 5.14 (b) The same spectrum as Fig. 5.13 (a) but expanded to show the small oxygen peak.
Fig. 5.15 An EELS spectrum of a thick section showing several plasmon peaks.
to separate the peaks. Fig. 5.17 is a WEDX spectrum of pure boron on a carbon film showing the problem of deconvoluting the boron from the carbon peak which in this case merge as one broad peak. The technique used here of ratioing everything to the oxygen concentration and using both WEDX and EELS methods avoids such problems. The copper and zinc peaks are separated at higher energy peaks not shown in Fig. 5.16. The presence of copper in the glass was disproven by using aluminium support grids instead of copper grids. In these tests no copper peak was observed proving that the copper peak resulted from the interference of the support grids.

The size of the oxygen peak varied greatly in relation to the size of the aluminium peak, the oxygen content (ignoring the boron) varying between the limits of 35 and 65% when corrected by a 'k' factor to take into account the X-Ray production efficiency factor; the detector efficiency factor and the sample efficiency factor. However, it was proposed that the extreme lower oxygen concentrations may have been inaccurate due to shadowing by the grid bars and thus the bulk of the higher values were taken as correct, giving the final analysis result in Table 5.2. No error limits are given in this table since although as mentioned above the EELS results are considered accurate to within 30% it would still imply in the most inaccurate analysis that the glass is boron rich with significant quantities of oxygen and
5.16 TEM WEDX Spectra of the Glass recorded on the film (above) and overhanging the film (below)
Fig. 5.17 WEDX Spectrum of boron on a carbon film.
aluminium present as well as trace quantities of the other elements given in Table 5.2.

<table>
<thead>
<tr>
<th>Element</th>
<th>Analysis (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Boron</td>
<td>88.7</td>
</tr>
<tr>
<td>Oxygen</td>
<td>6.3</td>
</tr>
<tr>
<td>Aluminium</td>
<td>2.8</td>
</tr>
<tr>
<td>Phosphorus</td>
<td>0.1</td>
</tr>
<tr>
<td>Sulphur</td>
<td>0.6</td>
</tr>
<tr>
<td>Calcium</td>
<td>0.2</td>
</tr>
<tr>
<td>Iron</td>
<td>0.6</td>
</tr>
<tr>
<td>Zinc</td>
<td>0.7</td>
</tr>
</tbody>
</table>

Table 5.2 Composition of the Glass as Determined by EELS and WEDX.

Further evidence for the accuracy of the analysis of the glass was provided by considering such cases as shown in the lower trace in Fig. 5.1 where there is no carbon background present and a good WEDX peak is observed. Calculating back from the EELS and WEDX results, an appropriate 'K' absorption factor for the boron would be about twenty times the k factor of aluminium. This is somewhat lower than the later work of Budd and Goodhew (137, 138, 139) who quote values of between 50 and 55. For the purposes of comparison diboron trioxide contains 27.5 wt% boron.

The production of an amorphous boron based precipitate in the brass was totally unexpected and it is appropriate at this point to consider how the formation of a boron glass is
possible. The chemical and physical properties of boron have been reviewed by Bower (140) and Matkovich (141). Boron is seen to form six crystalline polymorphs and one amorphous form. The crystallography of boron and its compounds is somewhat complex because of its ability to combine with itself to form large polyhedral structures. The icosahedron of boron atoms, for example, is a geometric form of cubic symmetry which has twenty equilateral triangular faces and twelve boron atoms at the vertices. This is referred to as the B12 unit which can group together to form larger units, such as that illustrated in Fig. 5.18 consisting of a central icosahedron surrounded by twelve others. The unit cell itself contains 84 boron atoms and is referred to as B84. Such open networks can accommodate one or more isolated foreign atoms to form stable structures such as MgAlB14 which would not be possible by simple ionic bonding.

Fig. 5.18 The Ideal Arrangement of Boron Atoms in the B84 Polyatomic Unit. (141)
The methods of preparation of amorphous boron have been discussed by Zhigach and Strasinevich (37). The essential condition to produce amorphous boron is temperature, boron produced by reduction of a boron compound at lower temperatures (900-1100K) is amorphous while those produced at above about 1100K are crystalline. Amorphous boron produced by a reduction technique contains typically 88-97 wt% B. Reduction of borax by aluminium results in a product containing 89 wt% amorphous boron, 7 wt% iron, 0.8 wt% iron and 2-3 wt% of an undissolved residue (37).

Batawi et al (142) and Morris et al (243) have detected amorphous B precipitates in melt spinning Cu-3B, Cu-7B and Cu-0.25Y-6B alloys. The amorphous boron particles were analysed using microdiffraction and EDX analysis. Their techniques showed no metal content within the amorphous particles and although the authors, "would not be surprised if the amorphous boron did contain some oxygen", no analysis was undertaken to confirm this (143).

Mattes, Marosi and Neidhard (145) meanwhile produced Cu$_2$Al$_{12.7}$B$_{104}$ under normal solidification conditions in a copper melt and Higashi and Takahashi (146) under similar conditions produced Al$_{0.7}$Cu$_{0.7}$B$_{25}$. Both products were crystalline.

There seems to be no reference in the literature to the production of amorphous boron under non rapid solidification conditions during the crystallisation of a copper based melt. The following chapter details experiments in casting
designed to gain information regarding the grain refining mechanism operating within the brass and in particular the effects of changing casting parameters upon the microstructure of the metal.
6. THE EFFECT OF CASTING PARAMETERS ON THE GRAIN REFINING ACTION

6.1 Mode of Addition and Concentration of Grain Refining

It was observed that the way in which the Al and B additions were made to the liquid brass was not important. The two elements could be added separately in powder or solid form, or as was usually done for convenience, in the form of Al-4B master alloy. Both additions were always necessary to produce the refining action. It was decided to investigate how an increase in the quantity of the master alloy would affect the refining action. A 60-40 brass melt was made and increasing quantities of masteralloy additions were made prior to a specimen being cast. These B additions took the form of Cu-B master alloy containing 2 wt% B. The aluminium concentration remained fixed at about 0.8 wt%. The specimens were then sectioned midway along their length prior to mechanical polishing and electropolishing. The effect of increasing the B concentration is shown in Fig. 6.1. The area of the fine equiaxed centre is seen to increase initially at the expense of the coarse equiaxed area. A maximum value is reached at about 0.02 to 0.04 wt% addition. Larger B additions are detrimental and additions of 0.22 wt% are seen to destroy the refining action in the ingot centre. This was seen to be accompanied by the appearance of hard particles within the brass. Such particles are shown after standard mechanical polishing in Fig. 6.2 (a) and after electropolishing in Fig. 6.2 (b). At the highest B concentration none of the previously observed feathery type amorphous precipitation were observed, whereas, in all other
specimens glass was found even in specimens with the higher B concentration where the hard particles were also present. These hard particles were seen to agglomerate within the brass. This made their extraction by replica techniques relatively difficult. However, successful replicas were made and the particles were seen to give a crystalline diffraction pattern (Fig. 6.2 (c)). They were also much too thick to analyse using the EELS technique but by assuming a 'k' B factor of 50 and using WEDX the spectrum in Fig. 6.3 was collected. The analysis results are given below in Table 6.1. These particles were richer in Al and Zn while

![Graph showing variation in size of the five-grained central region with increasing nominal boron addition.](image-url)

Fig. 6.1 Variation in size of the five-grained central region with increasing nominal boron addition.
Fig. 6.2 The Hard Particles Found in the Brass with Higher B Additions  
(a) Mechanically Polished  
(b) Electropolished
being poorer in oxygen. Thus, at higher B additions a crystalline B product was formed and the refining action producing the very fine grains was destroyed, although it should be noted however that there was some refinement of the structure with an equiaxed grain size of about 2 to 5 mm.

Fig. 6.3 WEDX Spectra of the Particles shown in Fig. 6.2.

6.2 Variation of Brass Composition

A section of the Cu-zinc phase diagram is shown in Fig. 5.3. Initial trials showed that the grain refining of brass with
the Al-B master alloy took place only around the 60-40 composition. Microprobe analysis of the bulk phases present in such a grain refined specimen showed the alloy to solidify with the Beta phase with alpha

![Element Analysis Table](image)

<table>
<thead>
<tr>
<th>Element</th>
<th>Analysis (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Boron</td>
<td>85.8</td>
</tr>
<tr>
<td>Oxygen</td>
<td>4.1</td>
</tr>
<tr>
<td>Sulphur</td>
<td>.4</td>
</tr>
<tr>
<td>Aluminium</td>
<td>7.3</td>
</tr>
<tr>
<td>Iron</td>
<td>0.2</td>
</tr>
<tr>
<td>Calcium</td>
<td>0.2</td>
</tr>
<tr>
<td>Phosphorous</td>
<td>0.1</td>
</tr>
<tr>
<td>Zinc</td>
<td>1.9</td>
</tr>
</tbody>
</table>

Table 6.1 WEDX Analysis of the Particles Shown in Fig. 6.2.

precipitating at the grain boundaries upon cooling. This is what would be expected from Fig. 5.3. Specimens with a nominal 0.8 wt% addition of Al-4B masteralloy were therefore cast with increasing zinc content starting from fully alpha brass, passing through the alpha-beta composition to the fully beta alloy. Composition intervals of about 2 wt% Zn were aimed for. This proved impossible to achieve accurately since the molten metal 'fumed' with large quantities of Zn vapour being lost in the atmosphere. However, a good range of results was achieved as given in
Table 6.2 where the composition ranges over which grain refinement was observed is also shown. The brass compositions have been normalised to 100%, impurities, sometimes present in very small concentrations, have been ignored and the B was naturally not detectable using ordinary microprobe techniques.

<table>
<thead>
<tr>
<th>Specimen No.</th>
<th>Cu</th>
<th>Zu</th>
<th>Al</th>
</tr>
</thead>
<tbody>
<tr>
<td>11A</td>
<td>75.3</td>
<td>24.2</td>
<td>0.5</td>
</tr>
<tr>
<td>11B</td>
<td>72.7</td>
<td>26.9</td>
<td>0.4</td>
</tr>
<tr>
<td>11C</td>
<td>69.2</td>
<td>30.5</td>
<td>0.3</td>
</tr>
<tr>
<td>12A</td>
<td>66.1</td>
<td>33.3</td>
<td>0.6</td>
</tr>
<tr>
<td>13</td>
<td>65.5</td>
<td>34.1</td>
<td>0.4</td>
</tr>
<tr>
<td>12B</td>
<td>65.0</td>
<td>34.5</td>
<td>0.5</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>118B</td>
<td>62.4</td>
<td>36.7</td>
<td>0.9</td>
</tr>
<tr>
<td>8B 8C</td>
<td>60.3</td>
<td>39.0</td>
<td>0.7</td>
</tr>
<tr>
<td>12C</td>
<td>60.3</td>
<td>39.1</td>
<td>0.6</td>
</tr>
<tr>
<td>14A</td>
<td>60.4</td>
<td>38.8</td>
<td>0.8</td>
</tr>
<tr>
<td>14B</td>
<td>57.7</td>
<td>41.5</td>
<td>0.8</td>
</tr>
<tr>
<td>14C</td>
<td>56.0</td>
<td>43.2</td>
<td>0.8</td>
</tr>
</tbody>
</table>

Table 6.2 Compositions and Structures of Brasses with 0.032 wt% B Addition. Specimen numbers given in Appendix.
The specimens of the 11 series all were of a fully alpha structure and no grain refining action was observed. Upon electropolishing a number of small particles became visible but none of the typical feathery amorphous precipitate was found (Fig. 6.4).

In the mid range of Zn concentrations from about 33 to 39 wt% zinc a well refined central region was observed of the type shown in Fig. 5.1. In all these specimens the feathery glass was observed, as has been discussed in the previous chapter. No significant change in the size of the refined area was observed across the range of Zn concentrations investigated. In some of the higher zinc brasses within this range (specimens 8B, 8C, 12C) elongated rod type and

Fig. 6.4 TEM Micrograph of a P particle seen in the Low Zinc Brass with 0.8 Al-4B addition.
Fig. 6.5 Specimens of Higher Zinc Concentration with 0.8 Al-4B Addition unetched (above) etched in ferric chloride solution (below).
Fig. 6.6 SEM Micrographs of Glass and Rod Type structures in Specimen 8B.
single particular structures were observed. Extraction replication of these particles gave a crystalline diffraction pattern in the TEM. The particles were, however, far too thick for reliable EELS analysis as shown in fig. 6.7 and WEDX analysis was undertaken using a B 'k' factor of 50. The results of this analysis are shown in Table 6.3. The oxygen concentration of the crystalline product is seen to be significantly lower than that of the glass quoted in Table 5.2. However, this may be due to experimental conditions in the TEM, only the EELS technique being able to give an accurate ratio of the boron: oxygen concentration. What is more important is to consider the oxygen content with regard to that of aluminium. This shows the glass to contain less aluminium and zinc relative to the oxygen concentration and compares favourably with the crystalline B product analysed in the specimens containing larger B additions shown in Table 6.1.

<table>
<thead>
<tr>
<th>Element</th>
<th>Glass</th>
<th>Rod</th>
</tr>
</thead>
<tbody>
<tr>
<td>Boron</td>
<td>78.0</td>
<td>85.1</td>
</tr>
<tr>
<td>Oxygen</td>
<td>15.4</td>
<td>3.7</td>
</tr>
<tr>
<td>Aluminium</td>
<td>3.6</td>
<td>7.4</td>
</tr>
<tr>
<td>Iron</td>
<td>1.6</td>
<td>0.5</td>
</tr>
<tr>
<td>Calcium</td>
<td>0.7</td>
<td>0.2</td>
</tr>
<tr>
<td>Zinc</td>
<td>0.7</td>
<td>3.1</td>
</tr>
</tbody>
</table>

Table 6.3 WEDX Analysis of the B Products found in Specimens 8B and 8C. Average of six spectra.
Fig 6.7 The best acquired EELS Spectrum of Rod type structure showing plasmon peaks (a) and (b) expanded scale to show indefinable oxygen peak L compared with fig. 5.14
Fig 6.7 (b)
In the specimens containing higher zinc contents (14A, 14B, 14C) a slight refining action was observed with a fully equiaxed structure of about 2 mm diameter. Specimen 14A was seen to contain a very small amount (approx. 5% volume fraction) of second phase, the other specimens both being fully beta phase. Upon electropolishing, these specimens revealed the presence of single particles fairly evenly distributed throughout the brass as well as smaller amounts of the glass structures. The glass was also evenly distributed throughout the brass and not just at the grain boundaries, as had been observed in the grain refined brass (Fig. 6.9).

Fig. 6.8 X-ray Diffraction Pattern of Rod Type Structure.
Fig. 6.9. Particles and Glass Found in the highest Zinc Brasses.
6.3 Effect of Recasting the Refined Alloy

The amount of superheat given to the melt prior to pouring had no effect on the refining action. Superheats of between 20K and 200K were used, the upper limit being imposed by the 'fuming' of liquid brass at high temperatures. Similarly, the length of holding time prior to casting was seen to have no significant effect. The refined brass could be recast with no obvious loss of refining as shown in Fig. 6.10 where the brass on the right was cast from the remelted brass on the left.

Fig. 6.10. Recast Brass showing No Loss of Refining Action.
A POSSIBLE GRAIN REFINING MECHANISM

Aluminium in combination with boron has been found to grain refine duplex brasses. This was confirmed in the present work. However fully alpha or fully beta brasses were not grain refined by the aluminium and boron under casting conditions identical to those employed in the grain refining of the two phase brasses.

Grain refined duplex brass had three distinct grain zones; an outer zone of fine chill crystals, an inner zone of very fine equiaxed crystals and a zone of coarser equiaxed crystals between the two (Fig. 5.2 (a)).

The lower zinc concentration fully alpha brasses did not show any significant refinement of structure upon addition of the boron and aluminium while fully beta brasses were seen to have a slightly refined structure with an equiaxed grain size in the centre of the ingot of some 2mm in diameter.

The grain refined material was seen to contain significant amounts of a boron rich glass which consisted primarily of oxygen and aluminium (Table 5.1). This glass had a feathery type structure and was distributed throughout the three zones of the grain refined ingot. In the very fine equiaxed central region the glass was clearly seen to mark the original beta grain boundaries which upon cooling became the nucleation and growth centres of the alpha phase. It was much more difficult to evaluate the position of the boron
rich glass prior to any solid state reaction in the coarser equiaxed areas due to the marked difference in scale of the two features. Fig. 7.1 (a) shows an electron micrograph of the electropolished coarse equiaxed

Fig. 7.1 (a) Coarse Equiaxed Grain structure of a Grain Refined Brass(60-40)

Fig. 7.1 (b) Glass-type Structure Found in Area of Fig. 7.1 (a)
region of a grain refined brass. Fig. 7.1 (b) shows a
typical glass structure within that coarse equiaxed region
and the difference in scale between the two illustrates the
problem of relating the position of the glass to the original
grain structure.

In the non-grain refined alpha and beta brasses crystalline
boron rich particles were found. Those in the alpha brass
were seen to give a crystalline diffraction pattern in the
TEM and to have a higher aluminium to oxygen ratio than the
glass. The precipitates were seen to be fairly evenly
distributed throughout the brass. The higher zinc brasses
of the beta type contained crystalline particles, sometimes
elongated in shape, again distributed fairly evenly
throughout the cast specimen. In common with particles
observed in the alpha brass, these elongated particles were
found to have a higher aluminium to oxygen ratio. The
transition between the grain refined two phase and fully beta
brass was characterised by the co-existence of both
crystalline boron products and boron rich glass, the amount
of glass decreasing as the zinc content increased. In the
non-grain refined fully beta brasses some of the glass was
observed but the quantity present was very minor compared to
the number of crystalline boron particles seen.

In both the grain refined and non-grain refined brasses boron
came out of solution upon solidification. This is not at all
unexpected when considering the low solubility of boron in
Fig. 7.2 The Copper Boron System (147)
copper, Fig. 7.2. Unfortunately, there is no available phase diagram data for the copper-zinc-boron system. Figure 7.2 shows the phase diagram of the copper-boron binary. This is expected to represent a reasonable guide as to what may occur in the ternary case in question. The boron is seen to have a very low solubility in solid copper, about 0.01 wt% at room temperature. This implies a very low distribution coefficient, \( k \), leading to a build up of the concentration of boron in the liquid ahead of the solidification interface and is consistent with what has been observed in all brasses investigated where boron was found in the form of discrete particles or, as observed in the very fine grain refined areas, at the grain boundaries. Indeed if boron had not come out of solution in such a manner then it seems very unlikely that such a good distribution of the boron products would have occurred, especially when the difference in density between the brass and the boron is taken into account. It is therefore concluded that the boron products, either crystalline or amorphous, were formed during the rejection of boron ahead of the solid-liquid interface. In the case of the low and higher zinc concentration brasses the rejected boron formed primarily discrete crystalline particles and in the case of the two phase brass the boron glass was formed.

The boron glass in the fine grained central zone of the grain refined two phase brass was seen to decorate very distinctly the original beta grain boundaries with its typical highly
branched structure. Considering the above argument its
final form or shape is not necessarily the one it adopted
during the operation of the solute rejection mechanism. As
described in Chapter 3 the rejection and redistribution of
solute ahead of the solidification front leads to a solute
enriched layer in the liquid and if this layer were enriched
enough in boron to be considered, for practical purposes, as
a boron layer then this would effectively form a film of
boron in the liquid ahead of the liquid-solid interface.
Films of amorphous boron surrounding a copper cellular
microstructure have been observed by Cookey and Wood (148,
149). The authors melt spun a Cu 2 wt% B alloy and observed
three distinct zones upon rapid solidification. The zone in
closest contact with the chill surface was featureless and
exhibited a maximum boron solubility; the central zone was
cellular equiaxed and contained boron rich particles while
the zone near the free surface formed a cellular type
structure surrounded by an amorphous boron film. These
various boron structures were explained by the authors (148,
149) as resulting from segregation and thermal processes.
Thermal treatment to bring the boron out of solution showed
that the overall boron concentration across the ribbon was
uniform. The author's (148, 149) further propose that the
amorphous boron observed in the films is "stabilised by
impurities and it must be assumed that any impurities are
pushed ahead of the solidification interface in zones 1 and 2
(the other two zones). In this case, the impurity is
likely to be oxygen from the surface of the copper powders
used in the preparation of the initial samples". Unfortunately the authors did not undertake any detailed microanalysis work to support this claim.

Further evidence of the immiscibility of boron in copper and its redistribution upon solidification has recently been published by Morris and Morris (150). They investigated the microstructure of melt-spun copper-silicon-boron alloys with varying silicon and boron concentrations. They found that while in Cu-Si-B and Cu-Si\textsubscript{3}-B\textsubscript{4} alloys the boron rich phase segregated in the form of boron rich particles, in the case of Cu-Si-B\textsubscript{6} and Cu-Si\textsubscript{2}-B\textsubscript{8} alloys the boron segregated in the form of continuous film, encapsulating the cellular copper-rich phase. In all cases the boron-rich phase was amorphous except in the Cu Si B\textsubscript{6} alloys where some crystalline products were observed along with the amorphous boron film. Their work is of particular significance to this investigation since not only have the authors observed amorphous boron formed by solute rejection at the solid-liquid interface in the form of a film, but they also observed crystalline boron products co-existing with the amorphous phase. Unfortunately, the authors offer no explanation as to how each phase is formed and offer no evidence of having positively identified or analysed the composition of the boron rich phases present with the melt spun ribbons.

In this investigation, however, the use of novel microanalytical techniques in combination with advanced electron
microscopy preparation techniques has permitted (it is believed for the first time) the accurate analysis of all the boron rich phases observed in the brass. The analysis of the glass (Table 5.1) and of the crystalline particles found in both the zinc rich brasses (Table 6.1) and in the copper rich brasses (Table 6.2) showed that the major characteristic difference between the two was the relative content of aluminium and oxygen. The glass was found to have a weight ratio of oxygen to aluminium of about 2:1 whereas the crystalline products had a ratio which ranged from 1:1 to 1:2. Indeed, in those specimens with a zinc content approaching a fully beta composition in which both amorphous and crystalline particles were found, the difference in the 0:Al ratio was seen to vary even more ranging from about 4:1 for the glass to 1:2 for the crystalline particles. It is always assumed that brass is a self-deoxidising alloy since the volatile zinc vapour which fumes from the melt also serves to reduce the amount of oxygen present in the melt (126). More recently though, it has been well demonstrated that brass melts do contain significant quantities of oxygen (127). An analysis of the boron products has shown that the boron reacts with oxygen in the melt to form the crystalline or amorphous product. This reaction with or absorption of the oxygen must take place as the boron is rejected ahead of the solid liquid interface. Our analysis indicates that if no oxygen was present in the melt then a crystalline boron product would be formed.
The aluminium quantities added, typically 0.8 wt% were always well in excess of the amounts found present within the glass and thus it may be concluded that the availability of the oxygen may be one of the controlling factors as to whether the amorphous boron product was formed. The presence of the amorphous phase was associated with grain refined casting. It is appropriate therefore at this point to consider why this should be so.

Identical casting conditions were employed in both the aluminium and boron grain refined brass and the non grain-refined brass containing no additions. Thus, of the various methods of grain refining discussed in Chapter 3.5, that is to say thermal, mechanical and constitutional, only a constitutional refining mechanism could have provided the observed refining action. The classical grain refining mechanisms of the constitutional type have been seen to rely on the production in or addition to the melt of many fine, favourable nucleation sites. The recently patented grain refining methods of Reif and Weber (110), described in Section 4.2, rely upon the production of nucleation centres (of unknown composition) in the melt of a copper based alloy after addition of, for example, an Fe-Mg-Zr-P master alloy. For the purposes of comparison a specimen of their grain refined brass was electropolished, using the standard orthophosphoric acid solution as described in Chapter 5, and observed in the SEM. A typical micrograph is shown in
Fig. 7.3 where a large number of particles can be seen throughout the relatively fine grained, equiaxed grain structure. This microstructure is therefore consistent with the classical grain refining theory based on heterogeneous nucleation.

This, however, is in sharp contrast to the observations of the brasses refined with aluminium and boron. Here the very powerful grain refining action in the central zone of the two phase brasses is associated with a grain boundary precipitate which is amorphous in nature. No profusion of particles within the grains was observed like those in Fig. 7.3 but only a boron product at the original grain boundaries. The precipitate was also amorphous and, as reported in Chapter 3,
glasses are typically bad nucleants, hardly wetting metals which explains why they are used in experiments to greatly undercool liquid melts. These two observations do not confirm what is required for a good nucleant. In view of our results a new grain-refining mechanism will now be proposed.

This mechanism is based on the enrichment in boron of the liquid ahead of the solidification front as illustrated in Fig. 7.4, see also Fig. 3.12 (b). For the purposes of this argument, the vertical scale in fig. 7.4 is marked boron concentration and ignores the presence of other solutes which may be enriched in the layer ahead of the solid-liquid interface. The value of the liquid concentration in boron $C_1^*$ for a 0.032 wt% addition of B to a 60-40 brass melt may be estimated from the Cu-B phase diagram Fig. 7.2. The value of $C_1^*$ is given by first calculating $T^*$ from similar triangles as shown in Fig. 7.5.

![Fig. 7.4 Boron Concentration Ahead of the Solidification front in the Freezing Brass at steady state at 1312K.](image-url)
\[
\frac{1084 - T^*}{1084 - 1013} = \frac{0.032}{0.05}
\]

\[\Rightarrow T^* = 1038°C\]

\(C_{1}^*\) is thus found from the ratio

\[
\frac{C_{1}^*}{2.54 - 0.05} = \frac{46}{72}
\]

\[\Rightarrow C_{1}^* = 1.63 \text{ wt}\%\]

The distance \(D_1/V\) in Fig. 7.4 may be estimated by taking \(D_1\) as \(10^{-9} \text{ m}^2/\text{sec}\) and \(V\) as 0.02 m/sec (the value of \(V\) being estimated from the observed freezing time of the cast ingots).

This gives

\[
\frac{D_1}{V} = \frac{10^{-9}}{0.02}
\]

\[= 5 \times 10^{-7} \text{m} \]

\[= 0.5 \mu\text{m}\]

Fig. 7.5 Simplified Schematic Representation of the Cu-B Phase Design Shown in Fig. 7.2
Thus at about 1312K a maximum boron concentration in the solute enriched layer of some 1.63 wt% should be expected if the boron behaves in the same way in the brass melt as it does in a pure copper melt. In the Cu-B melt solidification would proceed to give a large quantity of alpha solid solution based upon pure copper with a small amount of eutectic at the grain boundaries.

This boron enriched layer is observed in very fine grained areas in the refined brass. The fact that the boron forms an amorphous phase and that this phase is evenly distributed at the grain boundaries of the original beta grains raises the possibility that at some stage the amorphous boron formed a complete film around the growing beta crystal. As discussed in Chapter 3 the growth rate of a crystal depends on the nature of the s-l interface and is proportional to the liquid self diffusion coefficient. In the case of a growing beta brass crystal enveloped by a boron rich glass film within a liquid brass melt, the self diffusion coefficient of the Cu on Zn atoms within the liquid brass should be replaced by the value for the diffusion of Cu or Zn atoms within the boron rich glass.

Unfortunately, there are no diffusion coefficient data for Cu or Zn diffusion in amorphous boron glass reported in the literature but an estimate of such coefficients may be made by considering the Stokes-Einstein equation:
where $a_0$ is the atomic radius and $\eta$ is the dynamic viscosity of the material. This equation shows an inverse proportionality between the diffusivity and viscosity of a material. Again there is no published data on the dynamic viscosity of boron rich glasses but an estimate can be made from the data available for other glasses, see Fig. 7.6. It is perhaps most appropriate to use the value given for boron trioxide at 1120K since, chemically, this is the closest to the glass found in the brass and for the range of glasses shown it has the lowest viscosity and thus highest diffusivity which is likely to be an over-estimate providing that the boron rich glass can be considered a typical glass. The temperature of 1120K is approximately the equilibrium freezing temperature of a 60-40 brass as shown in Fig. 5.3.

![Fig. 7.6 The Viscosity of Some Oxide Glass Melts over a wide temperature range (151)](image-url)
The value of the dynamic viscosity of boron trioxide glass at 1120K is given in Table 7.1 along with the corresponding values for some liquid metals at their melting points. It can generally be seen that:

\[ \eta \text{ (Metal)} = \eta \times 10^{-4} \text{ (Glass)} \]

and thus at 1120K in the refined brass

\[ \frac{D_1 \text{ (Metal)}}{D_1 \text{ (Glass)}} = 10^4 \]

This implies that the growth rate of beta brass is significantly reduced due to the limited diffusion of copper and zinc to the solid-liquid interface. Concurrent with this reduction in growth rate, an increase in undercooling would be expected which would not only act to increase the growth velocity (slightly) but more importantly it would lead to an increase in nucleation rate. Such a scenario could explain the copious observed nucleation and limited size of grains seen in the central zone of the grain refined ingot.

<table>
<thead>
<tr>
<th>Metal</th>
<th>Viscosity (Pas) at M.P.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Silver</td>
<td>$3.88 \times 10^{-3}$</td>
</tr>
<tr>
<td>Cobalt</td>
<td>$4.15 \times 10^{-3}$</td>
</tr>
<tr>
<td>Copper</td>
<td>$4.0 \times 10^{-3}$</td>
</tr>
<tr>
<td>Iron</td>
<td>$5.5 \times 10^{-3}$</td>
</tr>
<tr>
<td>Nickel</td>
<td>$4.9 \times 10^{-3}$</td>
</tr>
<tr>
<td>Lead</td>
<td>$2.65 \times 10^{-3}$</td>
</tr>
<tr>
<td>Zinc</td>
<td>$3.85 \times 10^{-3}$</td>
</tr>
<tr>
<td>Glass</td>
<td>Viscosity (Pas) at 1120K</td>
</tr>
<tr>
<td>$\text{B}_2\text{O}_3$</td>
<td>31.0</td>
</tr>
</tbody>
</table>

Table 7.1 The Dynamic Viscosity of Metals at their Melting Point and $\text{B}_2\text{O}_3$ at 1120K (129).
The mechanism is summarised in Fig. 7.7 in five stages. The first stage shows the nucleated beta grains which grow in the second stage and form a boron solute enriched layer around the grains. This then forms the boron glass layer and slows down the growth rate down so that in stage 3 other grains are nucleated. In stage four the glass film breaks down in the last stages of solidification to form the observed highly branched structure at the beta grain boundaries and in stage 5 the solid state precipitation of the alpha grains at the original beta grain boundaries takes place.

The above mechanism would explain why the glass was associated with the grain refined specimens since if the boron rejected into the liquid at the solid liquid interface formed a discrete crystalline particle and not a film then there would not be any refining of the structure and boron particles would be found throughout the grain structure as was observed.

The above mechanism accounts for the very fine crystals observed in the central zone of the grain refined ingot. It is much harder to explain the existence of the three zones in the grained-refined ingot. It may be presumed that the outer zone of fine chill crystals is formed in the same manner as in the non grain refined ingot, i.e that the cold chill mould induced a high initial nucleation rate. The intermediate layer of coarser equiaxed crystals could be
nucleated by the chilling effect of the cold mould with respect to the melt but do not grow to the centre of the ingot to form the usual fully columnar structure. This implies that either there is nucleation taking place ahead of

---

Fig. 7.7 The Proposed Grain Refining Mechanism.

or that some other mechanism is operating which prevents their further growth into the liquid.
Since there were no observed heterogeneous nucleating centres in the coarser equiaxed grains the former argument nucleation ahead of the growing coarse equiaxed grains seems unlikely. Remembering that the boron glass has been also found in the coarse equiaxed crystals it could be postulated that the same growth restriction mechanism is operating there as proposed for the fine equiaxed central zone but that due to the higher temperature gradients and growth rates involved in the earlier stages of solidification of the ingot, dendritic growth is faster with a more lateral redistribution of boron taking place and that it is only after significant growth of the crystal has occurred that a sufficiently concentrated amorphous boron film can be formed to envelop the growing dendrite and inhibit the diffusion of copper and zinc to the dendrite surface. Thus, the grain refining mechanism would be expected to be less effective in the initial stages of ingot solidification.
8. CONCLUSIONS AND SUGGESTIONS FOR FURTHER WORK

8.1 CONCLUSIONS

1. Boron in conjunction with aluminium grain refines duplex brass. Under identical conditions alpha brass is not refined and beta brass slightly refined. The strong refining action observed in the duplex brass is characterised as having an outer layer of fine chill crystals and a very fine equiaxed central region separated by a layer of coarser equiaxed grains.

2. Amorphous boron is found at the original grain boundaries in the refined duplex alloy while the fully alpha and fully beta brasses containing boron and aluminium additions form a crystalline boron product. The crystalline boron product in the beta alloy is highly elongated and is found to coexist with the amorphous boron at the boundary of transition between the duplex and fully beta composition.

3. Combined WEDX and EELS is a powerful tool for boron analysis in the TEM. EELS overcomes the problem of the deconvolution of overlapping carbon and boron peaks observed in WEDX while WEDX is sensitive to any heavier elements present.

4. The amorphous boron was found to contain significant quantities of oxygen and aluminium. The crystalline boron products contained proportionately more aluminium and less oxygen than the glass.
There exists an optimum boron addition level (about 0.03wt% in the case studied) below which a smaller highly grain refined central region is observed and above which large, angular crystalline boron products are formed. The grain refining action in the duplex brass was reproducible upon recasting with no apparent loss of refinement.

There was no evidence for a potent heterogeneous-type of grain refining species being responsible for the grain refinement in the two-phase brass. However, the strong refining action was always associated with the production of amorphous boron.

**SUGGESTIONS FOR FURTHER WORK**

1. Further work needs to be undertaken to investigate the grain refining mechanism proposed in the light of the microanalysis results. A mechanism based on enhanced nucleation would be expected to present a lower undercooling before the onset of solidification. Similarly, a growth restriction mechanism would lead to greater melt undercoolings. This could be investigated by comparing the recorded cooling curves of grain refined and non-refined castings.

2. Directional solidification experiments could determine the conditions under which boron enriches the liquid ahead of the brass solidification front and to what extent. Interrupted directional solidification studies could reveal if it is
possible for the boron to form an integral layer in the liquid.

3. In all the solidification experiments the level of the aluminium was maintained at a fixed quantity. Although it is appreciated that aluminium is necessary for the grain refining to occur there is no evidence as to what role it plays. This could be investigated by fixing the boron, copper and zinc composition while varying the aluminium and observing its effect on the microstructure.
REFERENCES

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Appendix

Cast brass specimens used in this investigation.

Composition
n - nominal composition
a - analysed composition by EPMA

Only Cu, Zn, Al and B compositions are quoted, trace elements and impurities may make up remainder to 100wt%. Nominal additions may exceed 100% indicating, for example, a 0.8wt% Al addition to a 60-40 Cu-Zn brass.
Grain Refined Specimens Supplied by LSM and Investigated

<table>
<thead>
<tr>
<th>SPECIMEN</th>
<th>Cu</th>
<th>Zn</th>
<th>Al</th>
<th>B</th>
<th>OBSERVATIONS</th>
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<tr>
<td>90E</td>
<td>n</td>
<td>60</td>
<td>40</td>
<td>0.8</td>
<td>0.032 Reﬁned, Contained Glass, Used in Analysis</td>
</tr>
<tr>
<td></td>
<td>a</td>
<td>bal</td>
<td>40</td>
<td>0.55</td>
<td>0.013</td>
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<tr>
<td>92J</td>
<td>a</td>
<td>bal</td>
<td>33.9</td>
<td>0.96</td>
<td>0.016 Reﬁned</td>
</tr>
<tr>
<td>107G</td>
<td>a</td>
<td>bal</td>
<td>41.6</td>
<td>0.28</td>
<td>0.004 Reﬁned, Contained Glass, Used in Analysis</td>
</tr>
<tr>
<td>118B</td>
<td>n</td>
<td>60</td>
<td>40</td>
<td>0.8</td>
<td>0.032 Reﬁned, Contained Glass, Used in Analysis</td>
</tr>
<tr>
<td></td>
<td>a</td>
<td>bal</td>
<td>38.7</td>
<td>0.55</td>
<td>0.0143</td>
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Cast by NRG at LSM

121 n 60 40 0.8 0 - 0.22 Effect on Increasing Boron content, See Section 6.1 and Fig. 6.1
### Specimens Cast by NRG at Surrey

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<thead>
<tr>
<th>SPECIMEN</th>
<th>Cu</th>
<th>Zn</th>
<th>Al</th>
<th>B</th>
<th>OBSERVATIONS</th>
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<tr>
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<tr>
<td>2</td>
<td>n</td>
<td>60</td>
<td>40</td>
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<td>Not Refined</td>
</tr>
<tr>
<td>3 - 7</td>
<td></td>
<td></td>
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<td></td>
<td>Used for Development of Casting Practice at Surrey</td>
</tr>
<tr>
<td>SPECIMEN</td>
<td>Cu</td>
<td>Zn</td>
<td>Al</td>
<td>B</td>
<td>OBSERVATIONS</td>
</tr>
<tr>
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<td>----</td>
<td>----</td>
<td>-----</td>
<td>-----</td>
<td>--------------------------------------------------</td>
</tr>
<tr>
<td>8A</td>
<td>n</td>
<td>60</td>
<td>40</td>
<td></td>
<td>Not Refined</td>
</tr>
<tr>
<td>8B</td>
<td>n</td>
<td>60</td>
<td>40</td>
<td>0.8</td>
<td>0.032</td>
</tr>
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<td>39</td>
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<tr>
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<td>40</td>
<td>0.8</td>
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<tr>
<td></td>
<td>a</td>
<td>60.3</td>
<td>39</td>
<td>0.7</td>
<td>0.032</td>
</tr>
<tr>
<td>9A</td>
<td>n</td>
<td>60</td>
<td>40</td>
<td></td>
<td>Not Refined ) Used for )</td>
</tr>
<tr>
<td>9B</td>
<td>n</td>
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<tr>
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<td>SPECIMENS</td>
<td>Cu</td>
<td>Zn</td>
<td>Al</td>
<td>B</td>
<td>OBSERVATIONS</td>
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<td>-----------</td>
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<td>-----</td>
<td>-----</td>
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</table>
| 10        |     |     |     |    | Recast 8C  
|           |     |     |     |    | See Section 6.3  
<p>|           |     |     |     |    | and Fig. 6.10                    |
| 11A       | n  | 70  | 30  | 0.8| 0.032                            |
|           | a  | 75.3| 24.2| 0.5| Not Refined                      |
| 11B       | n  | 68  | 32  | 0.8| 0.032                            |
|           | a  | 72.7| 26.9| 0.4| Not Refined                      |
| 11C       | n  | 66  | 34  | 0.8| 0.032                            |
|           | a  | 69.2| 30.5| 0.3| Not Refined                      |</p>
<table>
<thead>
<tr>
<th>SPECIMEN</th>
<th>Cu</th>
<th>Zn</th>
<th>Al</th>
<th>B</th>
<th>OBSERVATIONS</th>
</tr>
</thead>
<tbody>
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<td>n</td>
<td>64</td>
<td>36</td>
<td>0.8</td>
<td>0.032</td>
</tr>
<tr>
<td></td>
<td>a</td>
<td>66.1</td>
<td>33.3</td>
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<td>Refined</td>
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<td>n</td>
<td>62</td>
<td>38</td>
<td>0.8</td>
<td>0.032</td>
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<tr>
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<td>a</td>
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<td>34.5</td>
<td>0.5</td>
<td>Refined</td>
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<tr>
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<td>n</td>
<td>58</td>
<td>42</td>
<td>0.8</td>
<td>0.032</td>
</tr>
<tr>
<td></td>
<td>a</td>
<td>60.3</td>
<td>38.1</td>
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<td>Refined, Contained Rods and Glass, Used in Analysis</td>
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<td>n</td>
<td>67.5</td>
<td>32.5</td>
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<td>0.032</td>
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<tr>
<td></td>
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<td>65.5</td>
<td>34.1</td>
<td>0.4</td>
<td>Refined</td>
</tr>
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<td>14A</td>
<td>n</td>
<td>58</td>
<td>42</td>
<td>0.8</td>
<td>0.032</td>
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<tr>
<td></td>
<td>a</td>
<td>60.4</td>
<td>38.8</td>
<td>0.8</td>
<td>Not Refined</td>
</tr>
<tr>
<td>14B</td>
<td>n</td>
<td>56</td>
<td>44</td>
<td>0.8</td>
<td>0.032</td>
</tr>
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<td></td>
<td>a</td>
<td>57.7</td>
<td>41.5</td>
<td>0.8</td>
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<tr>
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<td>n</td>
<td>54</td>
<td>46</td>
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<td>0.032</td>
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<td>a</td>
<td>56</td>
<td>43.2</td>
<td>0.8</td>
<td>Not Refined, See Fig. 6.5</td>
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</tbody>
</table>
Boron redistribution during solidification of a two phase brass

N R Gregg, P J Goodhew, and P M Budd
Department of Materials Science and Engineering, University of Surrey, Guildford GU2 5XH.

1. Introduction
Most metals are fabricated from the cast columnar and equiaxed state. Grain refinement by innoculation involves making additions to the melt promoting a more equiaxed grain structure which has a lower susceptibility to cracking and a more even distribution of any second phase present. Thus grain refined metals can withstand greater deformation rates during fabrication and possess improved mechanical properties.

2. Grain Refinement of αβ Brass with Al-4B Masteralloy
60-40 brass specimens with 0.8 wt% Al-4B masteralloy additions were cast with a 50-100K superheat into a graphite mould 38 mm diameter by 100 mm length. The non-refined cast structure is shown in the upper half of Figure 1 with columnar crystals radiating from the centre to the initial outer layer of fine chill crystals. The refined brass has a similar layer of chill crystals but then a coarse equiaxed structure is observed leading to a very fine equiaxed structure in the centre of the specimen. Metallographic and microprobe studies proved the refined brass to solidify wholly as β subsequently precipitating α at the original grain boundaries. The original β grain structure was shown to have a typical grain size of about 60μm in the very fine centre area. This represented a reduction of grain size of the order of X1000.

3. Microscopical Investigation
Standard metallographic techniques revealed not only the grain structure described but also a fine precipitate passing through the α grains and presumably at the original β grain boundaries, which was further revealed by electropolishing in 40% orthophosphoric acid at 2.2V (Figure 2). This precipitate had a feathery form and in addition certain globular artifacts were seen. Deeper electropolishing and subsequent extraction replication revealed further information (Figures 3 and 4). The precipitate was seen to grow from a globular centre with a coral or highly branched form. This structure repeatedly produced diffuse ring diffraction patterns and was therefore amorphous in nature.

4. TEM Microanalysis
Standard EDS analysis of extraction replicas of the glass on copper grids was undertaken. Many grain refined castings were investigated which significantly reduced the number of elements consistently found in the
glass, the purity of the initial melt being somewhat variable. The use of aluminium grids ruled out copper as a necessary constituent of the glass and windowless EDS analysis proved that oxygen is always present. A small boron peak was recorded (Figure 5) only from the regions which overhang the edge of the carbon support film by more than 2um (Figure 4), otherwise the boron peak was not observed presumably because of absorption in the support film and the overlapping of the adjacent boron and carbon peaks.

EELS analysis of the glass was used to obtain a boron to oxygen ratio and found to be on average 20:1 atom ratio (Figure 6). This was then used along with the average windowless EDS analysis to give the following analysis.

<table>
<thead>
<tr>
<th>Element</th>
<th>B</th>
<th>O</th>
<th>Al</th>
<th>P</th>
<th>S</th>
<th>Ca</th>
<th>Fe</th>
<th>Zn</th>
</tr>
</thead>
<tbody>
<tr>
<td>wt%</td>
<td>89.7</td>
<td>6.4</td>
<td>2.3</td>
<td>0.1</td>
<td>0.4</td>
<td>0.2</td>
<td>0.5</td>
<td>0.4</td>
</tr>
</tbody>
</table>

The accuracy of the EELS analysis with respect to the boron to oxygen ratio was investigated by analysing B$_2$O$_3$ on a carbon support film. The ratio was seen to vary between 0.67 and 0.9, the stoichiometric being 0.67. The errors associated with this analysis thus may vary by as much as ±30%, but even if the above analysis was at the boundary of these errors, the glass must be extremely boron rich. The strength of the boron and oxygen peak observed in the EELS and windowless EDS analysis illustrated the low sensitivity of the latter technique to boron. The presence of boron was also confirmed by SIMS, LIMA and Auger analysis. However these techniques do not have the resolution necessary when investigating such a fine artifact and are not so quantifiable.

5. Discussion of Results

Analysis of the glass has shown that boron, aluminium, oxygen and other minor constituents segregate to the growing $\beta$ crystal:liquid interface, where it is the last phase to solidify. The strong grain refining effect is produced by either constitutional undercooling or growth restriction mechanism. Constitutional undercooling has been discussed by Flemings and also Elliot but since pure aluminium or pure boron addition alone has no great effect, it seems that the glass plays a critical role. A proposed mechanism is illustrated in Figure 6, which relies on a solute enriched layer produced as a result of rejection ahead of the growing $\beta$ crystal then restricting the diffusion of copper and zinc atoms to the crystal and thus lowering the growth velocity. This would increase the melt undercooling and allow other nucleants in the melt to become operative. The presence of the coarser equiaxed outer grain structure can be explained by the greater cooling rate experienced in this region resulting in a greater growth velocity not permitting the build up of a stable growth restricting layer.

Work is continuing in the light of the analysis obtained.

Acknowledgements

The work was sponsored by the London and Scandinavian Metallurgical Co. Ltd., Rotherham and the SERC. The help of Miss D. Chescoe and staff of the Microstructural Studies Unit at the University of Surrey is gratefully acknowledged. Thanks are also due to Miss V. Kohler for the availability of LIMA facilities at Cambridge.
Applications of microanalysis

Fig. 1: Standard 60-40 Brass and grain refined 60-40 Brass cast with a 0.8% wt% Al-4B addition (below).

Fig. 2: Electropolished grain refined Brass.

Fig. 3: Extraction replica of the fine glass structure seen in Fig. 2.

Fig. 4: Extraction replica of the glass showing conditions under which an EDS Boron peak was recorded.
Fig. 5 Standard and windowless TEM EDS analysis of the glass illustrating how the Carbon peak absorbs the Bordon peak.

Fig. 6 EELS spectra of the glass.

Left - Fig. 7
1. Zinc, Aluminium, Boron, Oxygen and other minor constituents segregate ahead of the solidification front.
2. Here they form a solute enriched layer which impedes the diffusion of Copper and Zinc to the solid.
3. Grains meet.
4. Glass forms which branched structure.
5. Precipitation of α at former β grain boundaries. Glass runs through centre of α grains.

Literature
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