

The copper-boron eutectic – unidirectionally solidified

A. J. PERRY, A. R. NICOLL,† K. PHILLIPS*, P. R. SAHM†
Brown Boveri Research Center, CH-5401 Baden, Switzerland

The copper-boron eutectic is of the degenerate type requiring supersaturation for coupled growth. This has been achieved here through the use of high-temperature gradients (above 100 deg K mm⁻¹) in equipment designed to continuously cast a rod with a unidirectional structure. The eutectic is found to grow in three forms: globular, irregular flake-like to fibrous, and "Chinese Script". This last is the steady-state form, the crystal structure of which is β -rhombohedral. Tensile tests indicate a UTS of some 35 kg mm⁻² and a total elongation of about 20%. The electrical conductivity is about 83% that of copper.

1. Introduction

Copper-boron is typical of the type of eutectic which has been termed faceted/non-faceted [1], or, in the older terminology, an anomalous type [2]. This is evident from the appearance of the as-cast alloy, shown in Fig. 1a, which contains large areas of the irregular structure typical of uncoupled growth. Moreover, primary boron globules which are surrounded by a halo of primary copper indicate a eutectic which may degenerate, i.e. a so-called divorced or degenerated type of eutectic [3]. Under certain conditions,

however, the eutectic structure also crystallizes in a coupled manner (Fig. 1b).

The following experimental work reports the unidirectional solidification of copper-boron eutectic alloys together with measurements of their tensile strength and electrical conductivity. This work is to be understood as part of a series [4] of attempts to find a fibre-reinforced copper alloy with good electric conductivity.

Degenerate eutectics [3] are found typically in systems crystallizing with a faceted and a non-faceted phase. The two best known examples of

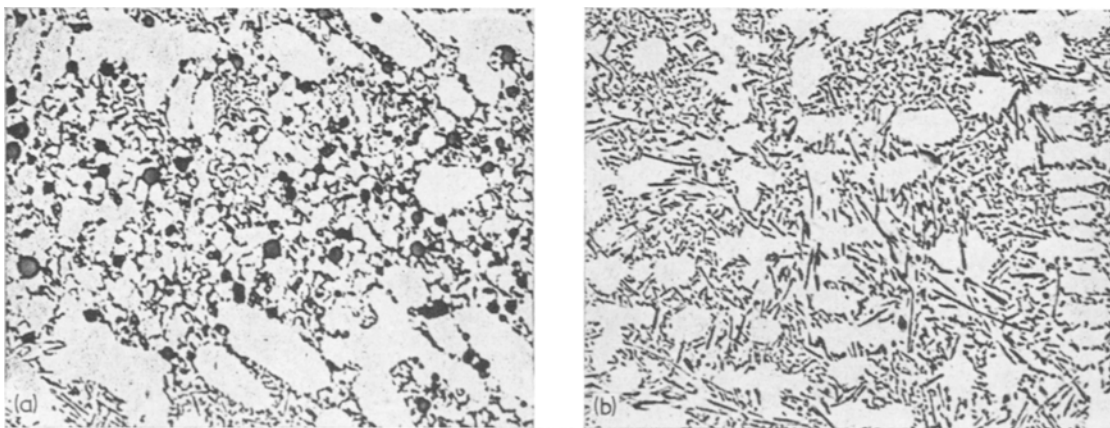


Figure 1 Microstructures of the as-cast copper-boron eutectic ($\times 280$) showing (a) globular boron and dendritic copper in areas of irregular eutectic – a degenerate structure; (b) regions of apparently better coupled growth in the same sample.

*Now in the Materials Science Division, School of Applied Sciences, University of Sussex, Brighton, UK.

†Now in the Brown Boveri Zentrales Forschungslaboratorium, D-6900 Heidelberg 1, Germany.

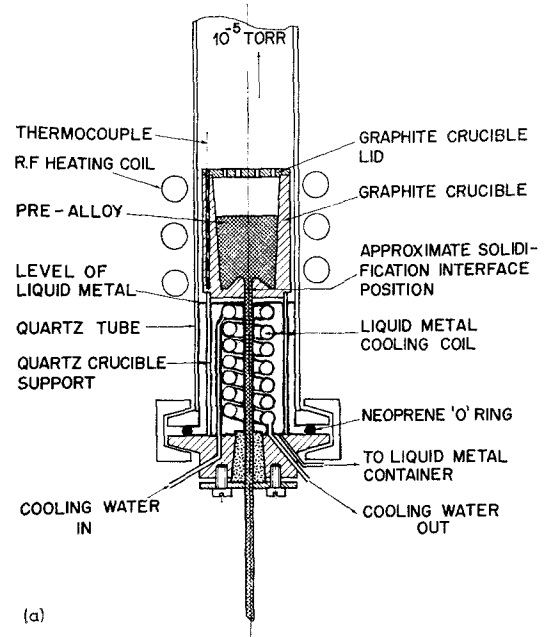
faceted/non-faceted systems [1] are the grey cast iron [5] and the aluminium-silicon [6, 7] eutectics. Of these two, the latter is particularly prone to degeneration, i.e. to forming large primary crystals of the faceted phase (silicon) which are surrounded by the primary matrix phase (aluminium) which, in turn, owing to its non-faceted character, appears dendritic. The reason for yielding primary crystals in an otherwise eutectic composition is sought in the difficulty of creating sufficient nuclei; this is tantamount to growing with a large supercooling. The non-faceted phase needs much less supersaturation and thus forms primary dendrites. To achieve coupled growth in these systems, stable conditions are required which enable a large supercooling to exist. This is most easily accomplished by high temperature gradients at the solidifying interface, i.e. keeping the supercooled region small. Therefore this work also reports a novel method of continuous casting with large temperature gradients.

The form of the copper-boron phase diagram was first established as eutectic by Lihl and Fleischl [8] who gave the second phase as a compound CuB_{22} on the basis of an unindexible X-ray diffraction pattern. Their interpretation was accepted by Smirjagin and Kvort [9] in their analysis of copper-rich alloys. The existence of this CuB_{22} phase was however questioned by Wald and Stormont [10] and its non-existence confirmed by both Rexer and Petzow [11] and Rao and Anderson [12]. The system is thus accepted as being a simple eutectic between copper and boron (solid solutions). The location of the eutectic point has been variously given [8-11]; the most recent determination, that of Rexer and Petzow [11], is $1013^{\circ}C$ ($1286K$) and 13.3 at. % boron (2.54 wt %).

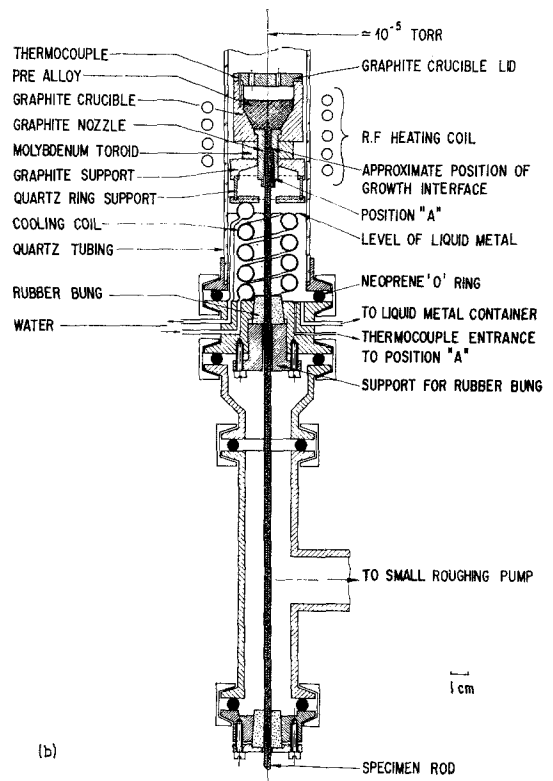
2. Experimental procedure

The equipment used here was developed to grow unidirectional structures through the use of a large temperature gradient. It was convenient to include the facility of continuous casting to produce a single rod which had been grown from one alloy but over a range of speeds in a step-wise fashion.

Early studies were carried out using the equipment shown in Fig. 2a. It was extensively redeveloped from that used [13] for continuous casting aluminium-carbon fibre composites. The features include direct RF heating of a graphite crucible in a vacuum of about 10^{-5} Torr. Further, the



(a)



(b)

Figure 2 Equipment developed for continuous casting the eutectic in rods of (a) 1.5 mm and (b) 4 mm diameter.

rod of about 1.5 mm diameter was taken from the bottom of the crucible into liquid metal [14] (gallium-indium eutectic, melting point 16°C) itself cooled with flowing water at 20°C. The experimental conditions were adjusted so that the solid-liquid interface of the grown rod remained in the nozzle indicated in Fig. 2a. The copper starter rod for the con-casting was nickel-coated to stop corrosion by the metal coolant. It was found that this system could produce directional structures based on the eutectic morphology shown in Fig. 1b; these are discussed below.

To produce samples the properties of which were more readily tested, a second piece of equipment was developed to continuously cast rods 4 mm in diameter. This equipment, shown in Fig. 2b, includes two further refinements over the first model. Firstly, a molybdenum toroid or collar was included in the crucible to enhance and stabilize the heating in the vicinity of the solid-liquid interface; a thermocouple was admitted into the extended nozzle (through position A in Fig. 2b) to check the local temperature at the interface. Secondly, the height of the liquid metal coolant was made variable: two levels were finally adopted, the upper one with the spacing between the solid-liquid interface and the coolant set at 15 to 17 mm and the lower one with a spacing of 33 to 35 mm. The temperature gradient was not measured but is estimated from the geometry and temperatures as being about 210 deg K mm⁻¹ for the upper level*. A series of growth speeds was employed ranging from 2.2×10^{-2} to 18×10^{-2} mm sec.⁻¹ This latter speed is not an upper limit, pure copper was grown at 29×10^{-2} mm sec.⁻¹ during the development of the equipment. It is worth remarking that a super-heat of some 100 deg K in the melt was needed for successful growth.

The alloys grown were made from OFHC copper of 99.97% purity and 99.99% pure boron mainly at the composition 2.54 wt% boron (the eutectic) but with some at the composition 2 wt% boron in addition. These were made up as pre-casts by melting the elements under argon in graphite crucibles and leaving them for some 30 min to ensure dissolution of the boron, which is very slow. The pre-casts for the equipment in Fig. 2b had a

4 mm diameter extension piece which was machined to a screw thread to couple with the nickel-coated copper starter rod.

The grown rods of 4 mm diameter were machined for conductivity and tensile testing as before [4] with a gauge length of 20 mm and a diameter of 2.5 mm; to avoid any possible ambiguity these specimens are nevertheless referred to as "4 mm diameter".

3. Eutectic morphology

As indicated in the introduction, copper-boron may be termed a degenerate eutectic. In this particular system three types of structure are evident as shown in Figs. 1a, 3 and 4. In Fig. 1a degeneration is made most obvious by the presence of boron globules each of which appears to grow from an individual nucleus, similar to the spherulitic growth of grey cast iron. Degeneration is also marked by the halo of primary dendritic copper around each such globule (Fig. 3). The rest-melt crystallizes with a seemingly irregular flake-like (to fibrous?) structure. The steady state structure appears to be of the "Chinese Script" type [16] yielding angular shapes that crystallize fibre-like over long distances, Fig. 4. This latter-type could only be stabilized at very high temperature gradients: of the order of 100 deg K mm⁻¹ or more with the equipment illustrated in Fig. 2b and medium growth rates. Our findings thus correspond to those of Hellawell [7] in the aluminium-silicon system.

The phenomenology of eutectic structures seen in these alloys may best be explained and summarized by using the "coupled growth concept" put forward by Kofler [17]. According to her theory and the later observations made by several workers, including Gigliotti *et al* [18] the copper-boron system should have a coupled zone of the type illustrated in Fig. 5, i.e. one not necessarily situated below the eutectic point (the coupled zone defines that range of composition in which the crystallization rate of both phases is equal so that coupled growth, i.e. normal eutectic growth, can take place).

Moreover, Gigliotti *et al* [18] have specifically stated, on the grounds of their own experimental observations, that the faceted/non-faceted type of eutectic should show the off-eutectic type of

*There is support for this value: in earlier work on the copper-CuZrSi eutectic [15] samples could be grown free of cells at rates v of up to only 1.60×10^{-2} mm sec.⁻¹ with the temperature gradient G of 64 deg K mm⁻¹ (i.e. G/v of some 4000 deg K sec mm⁻²). The same eutectic was grown at 5.55×10^{-2} mm sec.⁻¹ in the present equipment and found free of cells. The temperature gradient here must thus be above 220 deg K mm⁻¹.

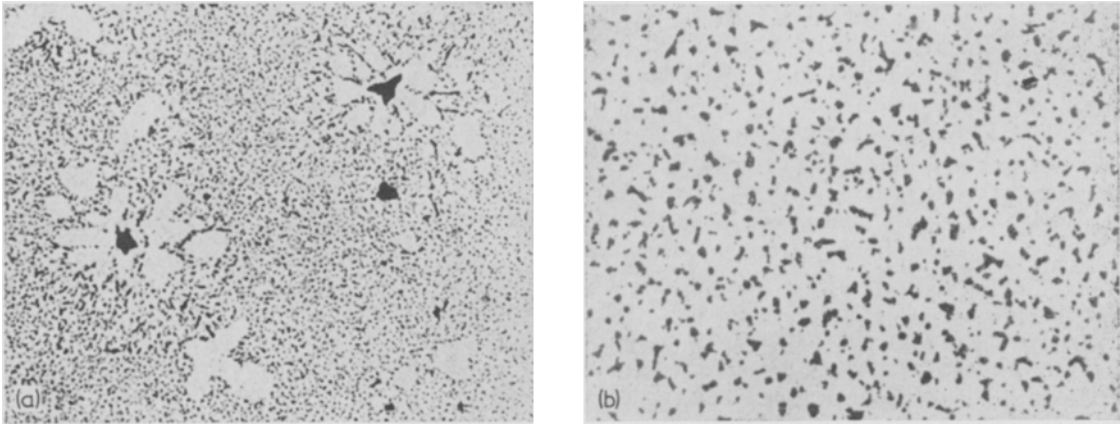


Figure 3 Degenerate eutectic structure shown in (a) primary boron enclosed in a halo of dendritic copper in a matrix of fine flake-like particulate boron ($\times 345$); this last shown in (b) at higher magnification ($\times 1050$).

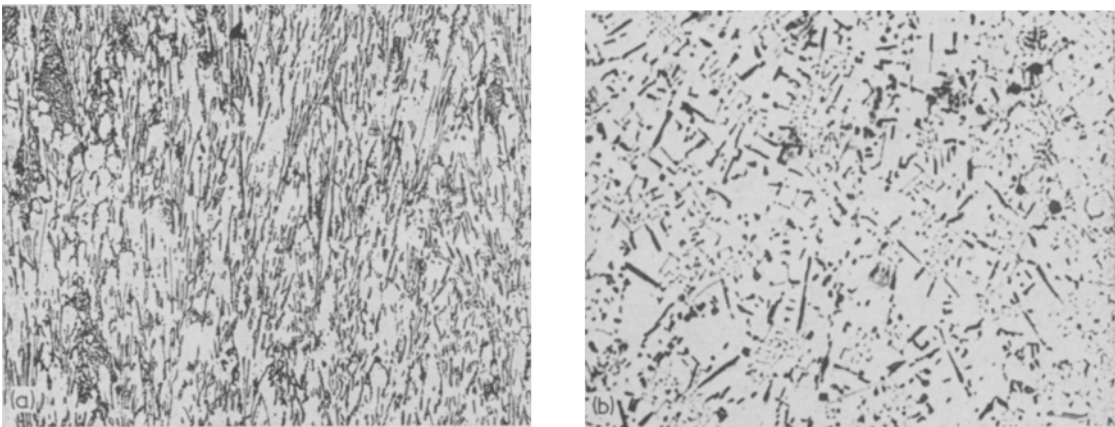


Figure 4 Microstructure of unidirectionally grown copper-boron eutectic showing the "Chinese Script" type of coupled growth (a) parallel ($\times 140$) and (b) transversely ($\times 325$) to the growth direction. The sample was 4 mm in diameter and grown at 7.08×10^{-2} mm sec $^{-1}$.

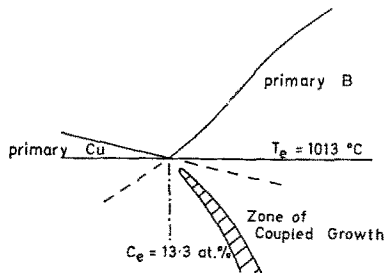


Figure 5 Part of the phase diagram of the copper-boron system [11] including a schematic representation of the region of coupled growth based on the proposals of Kofler [17] and Gigliotti *et al* [18].

coupled zone indicated in Fig. 5. Further, they expect halo formation of the non-faceted phase, here the copper, around the primary faceted phase, here the boron, as indeed observed (Figs. 1a and 3).

Once the faceted phase nucleates in a super-cooled melt of eutectic composition, the boron crystallizes as a quasi-primary crystal because the composition lies outside the coupled zone (Fig. 5). This creates an area of enriched copper melt around the boron globules which, in turn, causes copper dendrites to grow out from the primary boron (dendritically, because it is non-

faceted in character). The rest melt assumes the composition necessary for coupled growth (i.e. located within the coupled zone) and a normal eutectic structure may then form, Figs. 1b and 4. An irregular eutectic structure will form when both phases grow outside the coupled zone due to the presence of nuclei of both phases. The mixture of both types of structure, such as seen in Fig. 1, is therefore explained by simultaneous coupled and uncoupled growth of the eutectic.

The occurrence of the Chinese Script type structure (Fig. 4), which we consider the normal or coupled growth type in this system, at high temperature gradients means simply that a larger supercooling is stabilized, thus permitting crystallization within the coupled zone. Since

$$Gv = R_c,$$

where R_c is the cooling rate, the higher temperature gradients cause a higher cooling rate, which, in turn, favours a larger supercooling. Larger temperature gradients are known to make the growing interface less stable against fluctuations. Normally, fluctuations in interface temperature result in the formation of growth bands. A growth band very often requires fresh nucleation of one of the phases. Massive boron globules (Fig. 6) may have formed in this way in the small-diameter specimens. Also, a growth band may have caused the dissolution of boron precipitates and thus created small pieces which could act as nuclei when new crystallization sets in again.

4. Crystal structure of boron

Up to 1960, when the available data were critically reviewed by Hoard and Newkirk [19], many forms of boron were thought to exist. However, they concluded that only three modifications occurred in addition to an amorphous form. Later a fourth – the β -tetragonal type – was discovered. The polymorphs are listed in Table I. Their temperature stability has also been studied; Amberger *et al* [25] give the high temperature form – β -rhombohedral – as being stable at about 1400°C, β -tetragonal at 1100 to 1200°C and α -rhombohedral at lower temperatures. It has since been shown [25-28] that β -tetragonal is a carbon-stabilized lattice and further suggested [27] that the high-temperature β -rhombohedral form may also be impurity-stabilized.

In copper-boron alloys, the crystal structure of

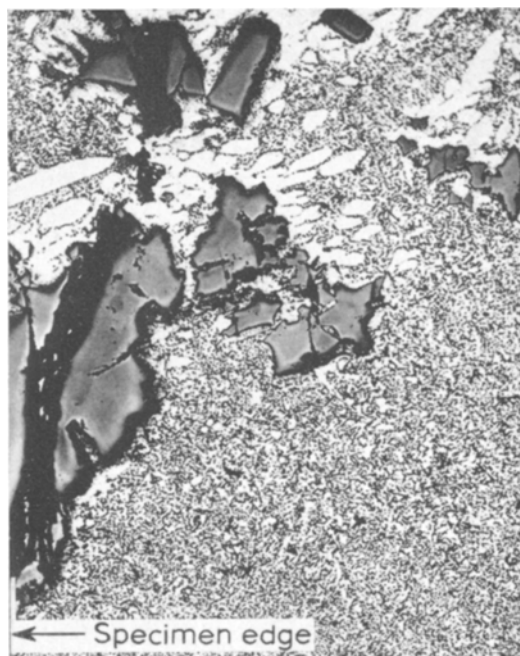


Figure 6 Typical massive boron found at the interface of the 1.5 mm diameter samples ($\times 68$).

the boron has been determined on two occasions. After 21 days at 1000°C, a copper-90 at. % boron alloy showed [10] mainly β -tetragonal X-ray diffraction lines but with both of the rhombohedral forms also present. A second high-boron alloy [11] was found to be β -rhombohedral after annealing at 950°C. The lattice parameters are included in Table I.

Here, the crystal structure of the boron after unidirectional solidification was determined by etching away the copper matrix from a 4 mm diameter sample containing the Chinese Script type structure (by immersion in concentrated nitric acid) and taking an X-ray diffraction pattern of the remaining boron. This etching procedure was made necessary by the low volume fraction of boron in the eutectic; in an X-ray diffraction pattern of a sample in the as-grown state, the copper reflections completely masked the boron pattern. Under these conditions the copper matrix had a lattice parameter of 3.607 Å as compared with 2.6153 Å listed by Barrett [29]. The structure of the extracted boron proved to be β -rhombohedral and the lattice parameters are given in Table II together with values obtained from the pure boron used in this study. The extracted boron had a slightly

TABLE I Crystal modifications and lattice parameters of Boron

Form	Reference	Lattice parameters (as listed by Amberger <i>et al</i> [25])	Density (g cm ⁻³)
Amorphous	Talley <i>et al</i> [20]		2.35 [20]
α -tetragonal (I) (B ₅₀ C ₂ etc)	Laubengayer <i>et al</i> [21]	$a = 8.75 \text{ \AA}$ $c = 5.06 \text{ \AA}$	2.39 to 2.44
(red) α -rhombohedral	McCarty <i>et al</i> [22]	$a = 5.06 \text{ \AA}$ $\alpha = 58.1^\circ$ (hex.) $a = 4.91 \text{ \AA}$ $c = 12.57 \text{ \AA}$	2.46
β -rhombohedral	Sands and Hoard [23]	$a = 10.14 \text{ \AA}$ $\alpha = 65.3^\circ$ (hex.) $a = 10.94 \text{ \AA}$ $c = 23.81 \text{ \AA}$	2.31 to 2.35
β -tetragonal (II)	Talley <i>et al</i> [24]	$a = 10.12 \text{ \AA}$ $c = 14.14 \text{ \AA}$	2.36 to 2.37
Cu-B alloys			
β -tetragonal	Wald and Stormont [10]	$a = 11.26 \text{ \AA}$ $c = 14.14 \text{ \AA}$	
β -rhombohedral	Rexer and Petzow [11]	(hex.) $a = 11.08 \text{ \AA}$ $c = 24.11 \text{ \AA}$	2.57

 TABLE II Lattice parameters of β -rhombohedral boron (hexagonal indices) found in the present work.

Pure boron	$a = 10.94 \text{ \AA}$ $c = 23.84 \text{ \AA}$ $c/a = 2.179$
Extracted boron from a unidirectionally solidified sample	$a = 10.95 \text{ \AA}$ $c = 23.85 \text{ \AA}$ $c/a = 2.178$

expanded lattice, as found by Rexer and Petzow [11], but our values show considerably less deviation from pure boron. As their studies were made on annealed unetched samples, it suggests that our etching procedure may have removed, to some degree, copper which was dissolved in the boron.

The crystal structure of the boron is interesting for two reasons. First, the β -rhombohedral allotrope is found regularly [10, 11] in copper-boron alloys. This would imply that copper is capable of stabilizing this crystal modification if the proposal [27] is correct that it is an impurity-stabilized form. Second, electron diffraction studies indicate the presence of β -rhombohedral crystallites [30] in amorphous boron fibres which possess high tensile strength and modulus. It is possible that the fibres in the present alloys may have similarly good mechanical properties as discussed in the next section.

5. Mechanical properties

Typical stress-strain curves for the 1.5 and 4 mm diameter rods are given in Figs. 7 and 8 respectively; this latter also includes a curve for annealed copper, taken from the present base material. The microstructures of these specimens are as follows: in the 1.5 mm diameter

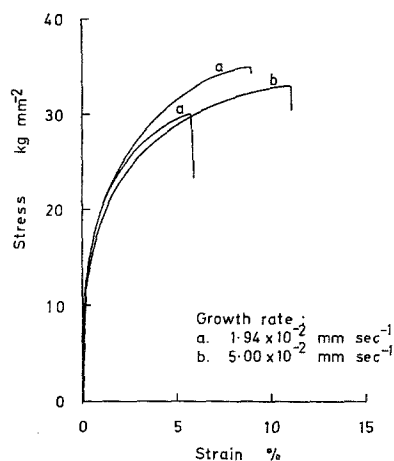


Figure 7 Stress-strain curves for 1.5 mm diameter specimens grown at various rates.

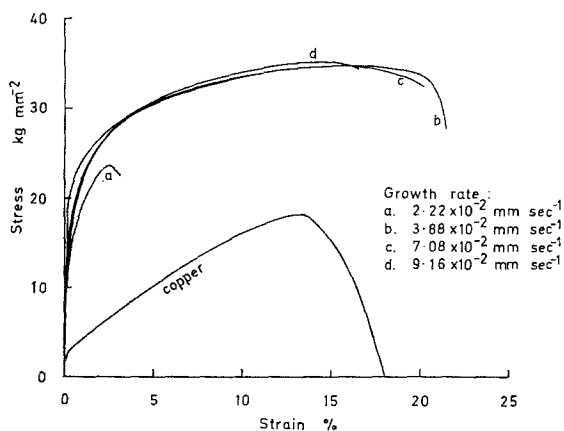


Figure 8 Stress-strain curves for 4 mm diameter specimens grown at various rates together with the curve for the pure copper starting material.

rods the structure was seldom the same throughout a given specimen and tended to include growth bands, regions of fine irregular globular boron (as in Fig. 3) and areas of directional fibrous boron. In addition pieces of relatively massive boron occurred near the outer surface (Fig. 6) as mentioned above. When tensile-tested, specimen failure was always associated with this massive boron which could be seen in the fracture surface; it was also cracked throughout the gauge length. The fracture was independent of whether the matrix was particulate or fibrous locally. In cases where it was fibrous, the fibres were multiply fractured only in the necked region; the lack of such fracturing in the remainder of the gauge length points to extensive ductility of the fibres.

In the 4 mm diameter rods, the microstructures were far more uniform and seldom included growth bands. In the case of fibrous-structured specimens, multiple fracture occurred throughout the whole gauge length (Fig. 9) as found in carbide-fibre reinforced nickel [31]. In non-unidirectional structures, fracture was associated with globular boron, the ductility being quite



Figure 9 Longitudinal section ($\times 430$) of a tensile sample taken from a 4 mm diameter specimen, after tensile testing, showing multiple fracture of the boron fibres. The sample was grown at 7.08×10^{-2} mm sec. $^{-1}$.

limited (e.g. the sample grown at 2.22×10^{-2} mm sec $^{-1}$ in Fig. 8).

Thus the low volume fraction of boron in the eutectic (6.90 vol %) is quite effective in strengthening copper, as shown in Figs. 7 and 8, either by dispersion-hardening (the fine globular form) or by fibre-strengthening. In particular, the yield point is raised quite markedly. The presence of coarse boron in any form leads to premature failure; in its absence total strains of the order of 15 to 20% are achieved.

Comparing the lack of multiple fracturing in samples which had failed prematurely with its extensive occurrence in highly ductile samples, one is led to the conclusion that fibre-strengthening is in vigour up to high strain values, the boron being capable of deforming plastically as remarked before. The change in regime from fibre strengthening to weakening is thought to be engendered by the work-hardening of the copper matrix (Fig. 8). As the fibres are ductile, fracture stresses can be developed, in both the fibre-strengthened and fibre-weakened conditions, which are greater than the fracture stress of the matrix alone, a situation which is discussed by Kelly [32].

An estimate of the strength of the boron fibres has been obtained in the following manner. In composites of boron filaments in an aluminium matrix, a breaking strain of 0.55 to 0.60% was observed [33], the mean breaking stress on the filaments being some 224 kg mm $^{-2}$. This value is low in the range of strengths normally observed for filamentary boron [33, 34], whose mean value is about 280 kg mm $^{-2}$, and underscores the weakening effect of a range of fibre strengths [13]. In the present work, at a strain of 0.6% the stress on the composite is about 20 kg mm $^{-2}$ (Fig. 8), corresponding to 185 kg mm $^{-2}$ on the boron, from the "law-of-mixtures" relation [32]. This estimate assumes that the fibres are infinitely long and parallel to the tensile axis and also that all the boron in the eutectic is in fibrous form. It is clear from Figs. 6 to 8 that these conditions are not met, so that the actual strength of the fibres is higher and possibly close to the value quoted above for individual filaments.

6. Electrical conductivity

The electrical conductivity is given in Fig. 10, plotted against the ultimate tensile stress (UTS) as ordinate, for both the 2 and 2.54 wt % (eutectic) boron alloys. The differences between

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