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The properties of directionally-solidified eutectic and hypo-eutectic copper-zirconium alloys

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Alloys of the copper-Cu_5Zr eutectic have been directionally solidified over a range of growth rates. The tensile strength was found to be high, 0.6 to 1.0 GN m^{-2}, in contrast to the poor electrical conductivity, typically 22 m Ω^{-1} mm^{-2}. In order to improve the latter at the expense of the former, hypo-eutectic (copper-rich) alloys were also studied. Alloys of composition in the region of copper-4 wt % zirconium possessed a useful combination of properties but these were not superior to the properties of conventionally cast samples. These alloys were shown to be stable against exposure to elevated temperatures.

1. Introduction

Current interest in copper-zirconium alloys stems from the work of Saarivirta and Taubenblatt [1, 2] and Dies and Jung-König [3, 4]. They showed that low-alloyed copper could be precipitation-hardened to produce a material with good electrical and mechanical properties. In contrast to most alloys strengthened in this way, their alloy has a reasonable capacity for retaining mechanical strength after extended periods at elevated temperatures. Subsequent work has extended to studies of the effect of further alloying elements [5, 6] and of internal oxidation [7] on the properties of these alloys.

An alternative way of strengthening copper is offered by fibre reinforcement. One way of achieving this is through the directional solidification of a copper-base eutectic alloy. Such an approach produces a structure which is in equilibrium and is therefore not prone to softening at elevated temperatures. A further advantage is that material can be used in the as-solidified state and form, except possibly for a heat-treatment to precipitate out any of the strengthening phase retained in the copper solid solution after the solidification process.

Previous work on directionally-grown copper-base eutectics has been concerned with copper-chromium alloys [8, 9] which have a low volume fraction of second phase, copper-Cu_2O alloys [10, 11] where the fibres break up under stress to give dispersion-hardening, and the copper-Cu_2S system [12] which tends to globularize during cooling. In contrast to these rather discouraging results, work by Cline and Stein [13] on the lamellar copper-silver eutectic showed it to have a yield-stress considerably higher than the pure components.

The phase-diagram of copper-rich copper-zirconium alloys as given by Pogodin *et al* [14] and Raub and Engel [15] in Hansen's Handbook [16] is a simple eutectic with copper in equilibrium with an intermediate Cu_3Zr phase. The eutectic point is to the copper-rich side. The system seemed a promising one for directional solidification: the volume fraction of copper (from which virtually all zirconium can be precipitated [1, 3]) indicates sufficient conductivity, the volume fraction of second phase is high enough to expect reasonable mechanical properties. A parallel study [17] of the equilibrium diagram has shown, however, that the volume fraction of copper in the eutectic (which is formed with a Cu_5Zr phase) is considerably less than was originally thought. In order to achieve reasonable electrical conductivity values we have studied not only the properties of the eutectic but also of copper-rich hypo-eutectic alloys which have been directionally solidified.

2. Experimental procedure

All alloys made in this work were based on

99.93% pure OFHC copper and zirconium of 99.99% purity. Pre-alloys were made following the method outlined elsewhere [18] and directionally solidified following the same procedure with a temperature gradient of 64 K mm^{-1} at the solid/liquid interface and a molten zone some 20 mm long. In addition, the electrical conductivity was determined ($\pm$ 0.1%) parallel to the growth direction at the standard temperature of 293 K using equipment designed and built by Mr O. E. Lanz of this laboratory.

As discussed below, a number of samples were vacuum heat-treated. In these instances the electrical conductivity was determined both before and after heat-treatment. At the end of such a treatment all samples were furnace-cooled.

3. Results and discussion

3.1. Eutectic alloys

The eutectic, formed between the copper solid solution and an intermediate Cu_5Zr phase [17], is of the lamellar type [1, 19] as shown in Fig. 1a. The volume fraction of copper has been determined:

transverse section	42% $\pm$ 7%
longitudinal section	46% $\pm$ 6%

based on an analysis of 150 fields from each using a Quantimet 720. The variations are attributed to changes in orientation of the eutectic*. The theoretical density of the Cu_5Zr phase, as calculated from the transverse section value, is 7.86 g cm^{-3}.

During directional solidification, the intermediate phase grows slightly ahead of the copper as can be seen in the quenched interface shown in Fig. 1b (achieved using the equipment of Sahm and Lorenz [20]); the build-up of copper ahead of the Cu_5Zr is evidenced by the fine copper precipitates seen in the quenched liquid. At the highest speed used here, colony formation was found to occur (Fig. 1c) with the characteristic coarsening at the cell boundaries.

The lamellar spacing λ varied with the growth rate v and is compared in Fig. 2c with the standard relation [21]

$$\lambda^2 v = \text{constant}. \qquad (1)$$

The effect of directional solidification on the mechanical properties can be seen in Fig. 3; both the fracture stress and strain were increased relative to the as-cast (non-unidirectional) condition. As shown in Fig. 2b, the fracture stress depends strongly on the growth rate (i.e. the inter-lamellar spacing) whilst the fracture strain varies relatively little. No necking of tensile specimens was noted and no cracking of the lamellae occurred behind the fracture surface which cuts cleanly through both phases as shown in Fig. 1d.

Directional solidification also improves the electrical conductivity (Fig. 2a) in comparison with the as-cast state. The conductivity is practically independent of the growth rate, being some 37% that of copper, that is, roughly the same as its volume fraction. Taken in conjunction with the improvement over the as-cast values produced by directional solidification, the results can be interpreted as meaning that the Cu_5Zr phase is a poor conductor so that conductivity depends only on the volume fraction and the continuity of the copper lamellae.

Some specimens were heat-treated for 100 h at 773 and 1173 K. Their tensile properties and electrical conductivity are included in Fig. 2, where it is seen that the structure is indeed quite stable against thermal exposure at 773 K but loses strength at 1173 K, falling to the level of the as-cast material.

3.2. Copper-rich hypo-eutectic alloys

The present work was initiated with electrical conductor applications in mind. The eutectic discussed above is remarkably strong but poorly conducting (i.e. a conductivity of some 37% that of copper), so it seemed a reasonable approach to adopt to sacrifice some strength in favour of an improved conductivity by directionally solidifying hypo-eutectic alloys. We have studied the properties after solidification at only one speed, namely 5.32 $\times$ 10^{-2}mm sec^{-1}, reasoning that the strength could be increased simply by increasing the growth-rate.

Included in Fig. 4 are the electrical and tensile properties of the hypo-eutectic alloys in the as-grown state. The volume fraction of eutectic was estimated in each specimen in a transverse section taken just behind the fracture surface (an example is given in Fig. 5a). Included in Fig. 4c is the inter-lamellar spacing which is found to depend on the alloy composition. As the lamellar spacing is normally found [31] to be a unique function of growth speed (Equation 1), this is taken to mean that this interdendritic eutectic does not solidify at the growth rate imposed by the equipment. The effect is not understood.

The tensile strength of the alloys falls as the

*This analysis was carried out by Mr. I. Brough at the University of Manchester Institute of Science and Technology.

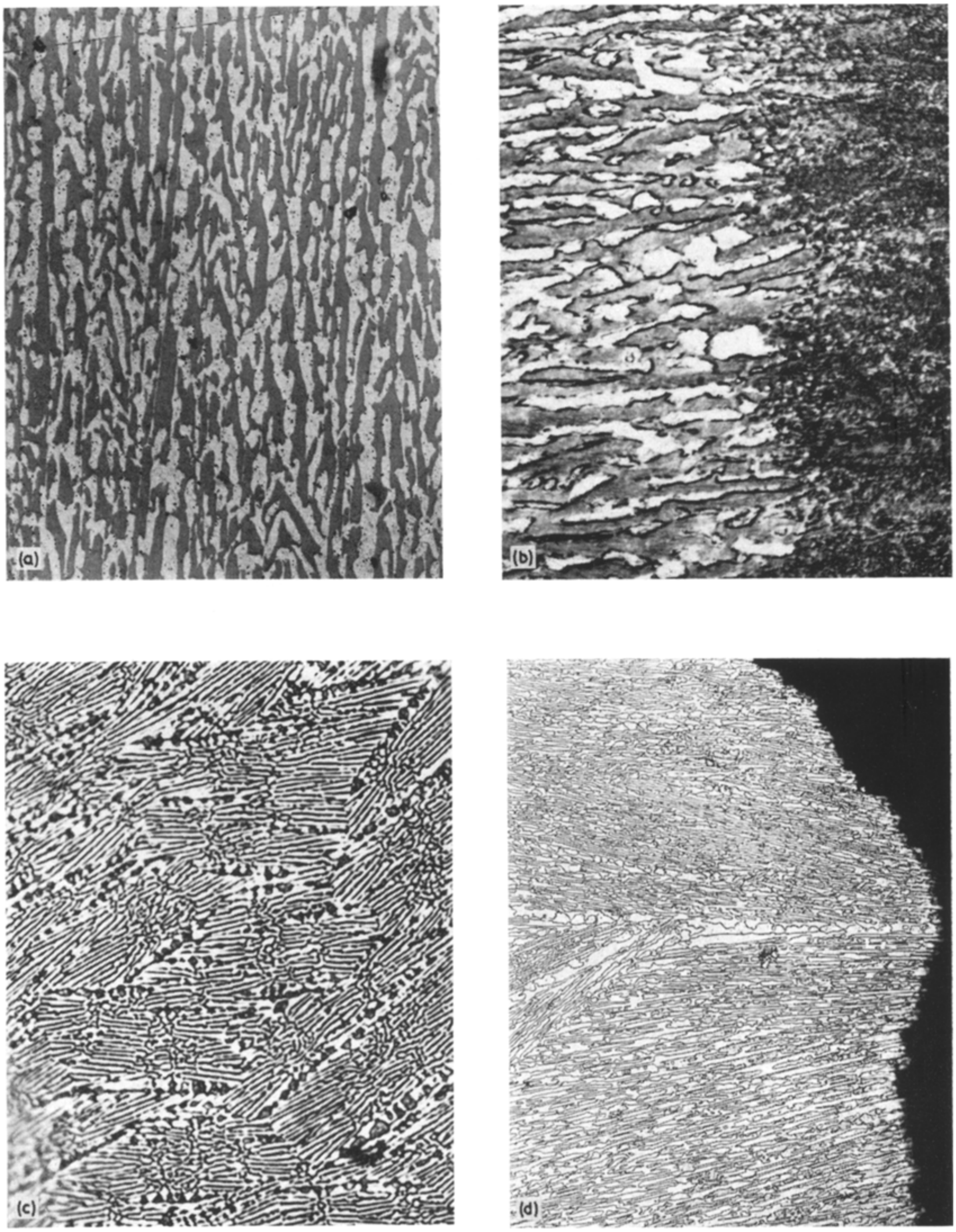

Figure 1 (a) Longitudinal microsection of the eutectic showing the lamellae of copper (light) and the intermetallic Cu_5Zr phase in the unetched condition ($\times$ 560). (b) Longitudinal section of a quenched interface showing the intermetallic lamellae growing slightly ahead. The build-up of copper in the liquid alloy ahead of this phase can be seen from the very fine copper globules ahead of the interface in the quenched liquid ($\times$ 840). (c) Transverse section of a sample grown at 0.53 mm sec^{-1} showing the colony structure ($\times$ 1680). (d) Etched longitudinal section of a fracture surface showing the lack of cracking behind the fracture which cuts cleanly through the sample ($\times$ 420).

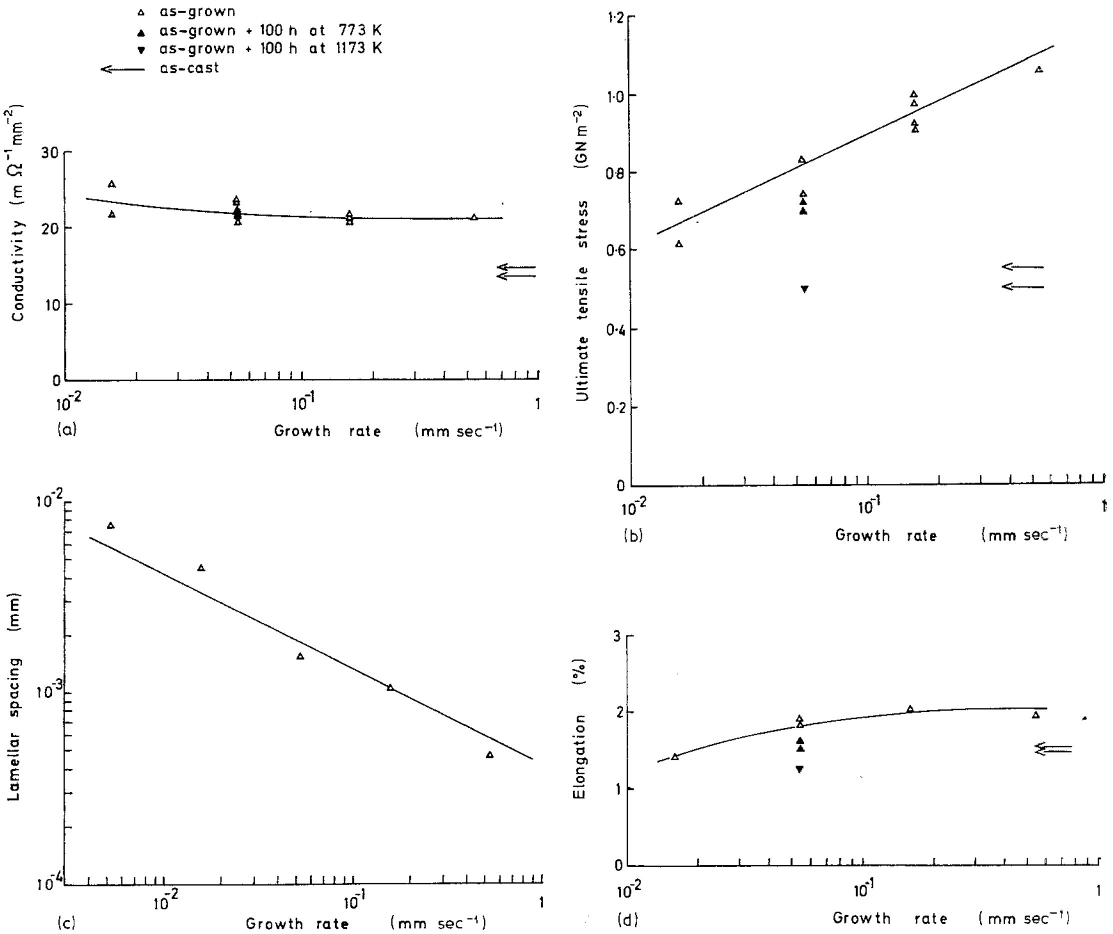

Figure 2 The (a) electrical conductivity, (b) ultimate tensile strength, (c) lamellar spacing and (d) elongation to fracture, of the eutectic as a function of growth speed before and after heat-treatment. Included are the results of as-cast samples.

copper content is increased. In contrast to the eutectic alloys, some samples (Fig. 6) exhibited a mechanical instability, i.e., necking, beyond the fracture strain of the eutectic and extended still further before fracturing. The elongation to fracture indeed increases as the copper content increases, as is seen in Fig. 4d. Only in the necked region had the eutectic cracked, presumably at the point of mechanical instability, then formed voids as shown in Fig. 5b. The voids do not extend into the dendritic copper, arguing a degree of fracture-toughness not possessed by the eutectic. The eutectic in the present alloys thus seems to have fractured at strains much greater than in the simple eutectic samples where cracking leads to catastrophic failure. It may be that the fault frequency in the hypo-eutectic alloys is less. If we associate failure of the eutectic with a mechanical instability leading to cracking because the material does not deform plastically and neck, then an alternative explanation is offered by the theory of Mileiko [22] (substantiated in copper-tungsten composites [23]) that a constraint exercised by the copper retards the onset of mechanical instability.

The conductivity of the samples in the as-grown state was not as high as anticipated and the discrepancy was attributed to Cu_5Zr dissolved in the copper; the extent of this would probably be greater at higher copper levels because of the greater diffusion distance to the eutectic lamellae. A precipitation heat-treatment was imposed and coupled to tests of the stability of the structure against exposure to elevated

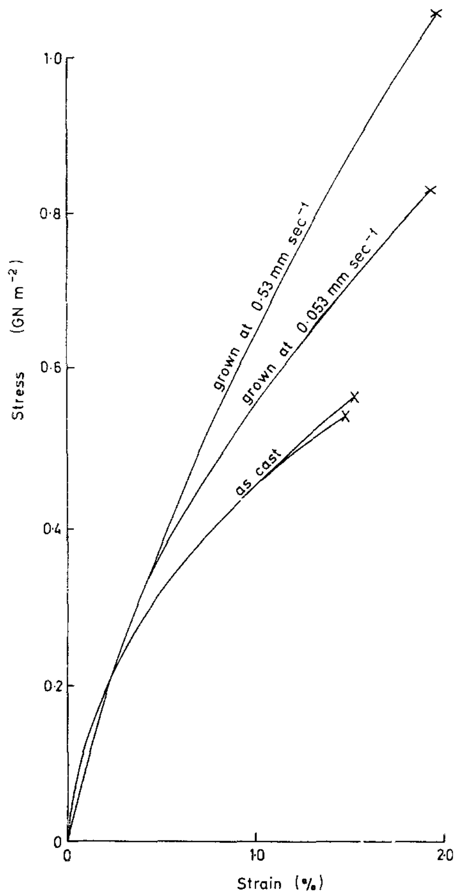

Figure 3 Tensile curves of directionally solidified and as-cast samples.

temperatures (see below).

Although there is some disagreement in the literature [1, 24-26] as to the precise solvus, there is generally thought to be negligible solubility below 773 K. It has been shown that 1 h at this temperature is sufficient to precipitate out the dissolved phase from dilute alloys, with [1] or without [3] prior cold-work. This heat-treatment was therefore applied to one alloy (i.e., two specimens) and the conductivity was found to be markedly improved. A series of samples of differing copper contents was then held at the same temperature of 773 K for 100 h. A comparison (Fig. 4a) between the results from the two sets of specimens shows that 1 h is indeed sufficient for precipitation. Finally the samples from the short heat-treatment were held at 1173 K for 100 h (the eutectic temperature is 1244 K) and the conductivity was found to be unchanged.

The rather complicated form of the conductivity-composition relation (Fig. 4a) is thought to be related to the low volume fraction of copper in the eutectic itself. It would seem likely that a significant improvement is only achieved when the copper matrix is continuous, the copper enclosed by the Cu_5Zr being blocked off. The conductivity of the Cu_5Zr phase is thus implied as being low. As the conductivity-composition curve is not linear, we cannot obtain a measure of its conductivity using the parallel conductor model [27] in which total conductivity is assumed to be proportional to the volume fraction and conductivity of each component (i.e., a law of mixtures).

The tensile properties were determined after both of the 100 h heat-treatments. As shown in Fig. 4b, the strength after heat-treating at 773 K is somewhat higher than in the as-grown condition, whilst after treatment at the higher temperature, the tensile strength is the same as in the as-grown state. The heat-treatment causes the Cu_5Zr retained in solution during the growth of the samples to precipitate out as shown by the conductivity data. The difference between the tensile properties after the two types of heat-treatment is attributed to a difference in the mode of precipitation. At 773 K precipitation is though to occur in the copper, thereby hardening it; the heat-treatment corresponds to that used to precipitation harden low-alloyed copper-zirconium [1-4]. Such matrix-hardening has also been reported [28] in directionally-grown aluminium-Al_2Cu eutectic alloys. At the higher temperature of 1173 K precipitation is thought to occur on the existing Cu_5Zr lamellae. As the volume fraction of the lamellae is hardly increased by such precipitation the tensile properties remain ostensibly the same as in the as-grown condition. It should be added that solution-strengthening of the copper by the Cu_5Zr dissolved in it is negligible [1].

Included at 773 K for 100 h were two specimens of an as-cast (non-unidirectionally) copper-4 wt % zirconium alloy; the conductivity and tensile strength are given in Fig. 4. As seen, and in contrast to the eutectic itself, the as-cast material exhibits properties which are not inferior to those found in the unidirectionally grown state. This means that the improvement in properties caused by directional solidification at a relatively slow rate is balanced by an improvement attributable to the fineness of the structure in a conventionally-cast sample.

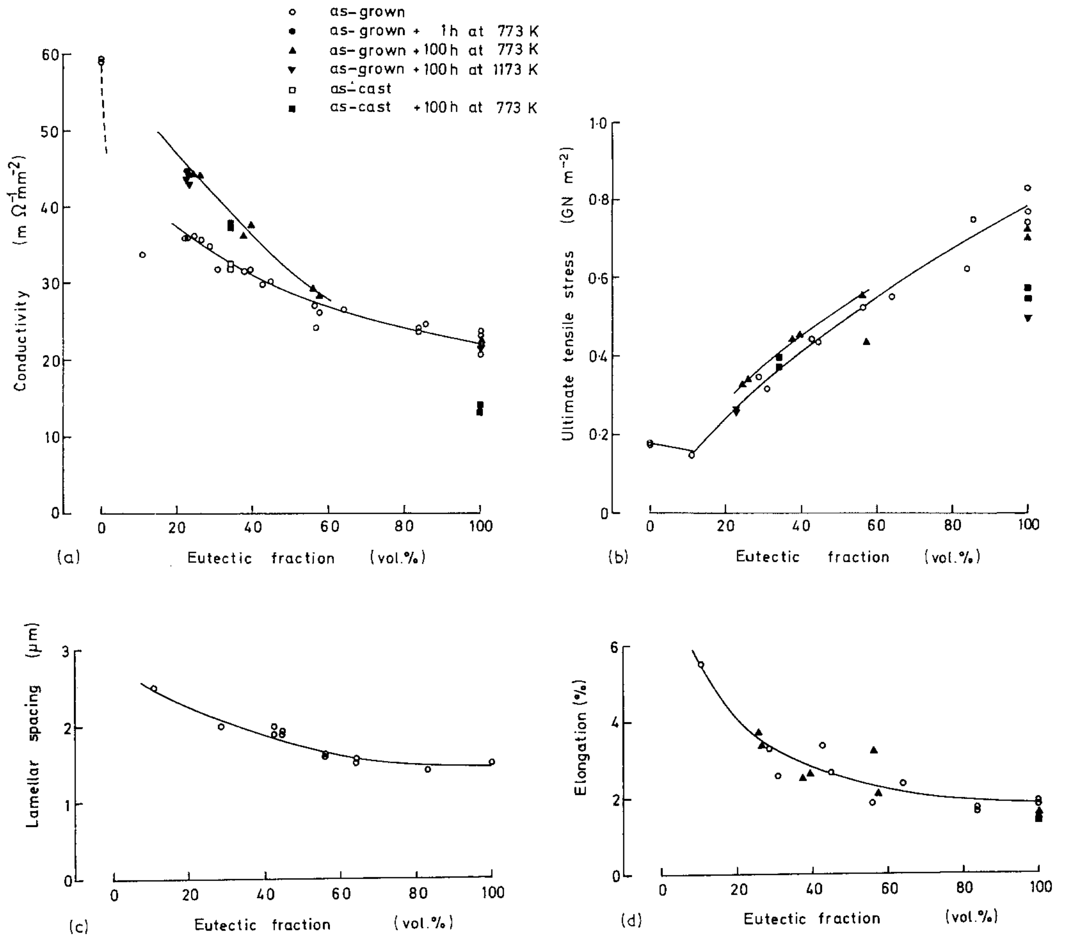

Figure 4 Properties of hypo-eutectic alloys in the as-grown (5.32×10^{-2}mm sec^{-1}) and as-cast states, before and after heat-treatment, as a function of the volume fraction of eutectic. This was estimated in the as-grown samples from microsections taken behind the fracture surface. The dashed curve included in (a) is the variation of conductivity with zirconium content in copper solid solutions after Saarivirta [1].

A further feature of the results is the curvature in the UTS-eutectic fraction data given in Fig. 4b. It was shown in the previous section that the tensile strength is quite strongly dependent upon the growth rate, presumably through its effect on the lamellar spacing (a dependence of the flow stress on the inverse square root of lamellar spacing has been established [13, 29]). The increase in lamellar spacing at low eutectic volume fractions shown in Fig. 4c carries with it a weakening of the eutectic itself. The weakening of the composite leads to a downward curving relation between the UTS and the eutectic volume fraction as the latter is decreased.

There is a unique relation between the volume fraction of eutectic (which can be estimated metallographically) in the hypo-eutectic alloys and the zirconium content (which can be analysed chemically). The relation [30] depends *inter alia* on the density of the Cu_5Zr phase, which was estimated in the previous section, and this theoretical curve is given in Fig. 7. A comparison between samples which were both chemically and metallographically analysed on the one hand and this theoretical curve on the other indicates a quite reasonable agreement. The chemical analyses show a discrepancy to exist between the weighed-in and as-grown compositions. The loss of zirconium is attributed to a zone-refining effect during directional solidification. Some of the lower melting-point eutectic (which contains the zirconium) is zone-refined

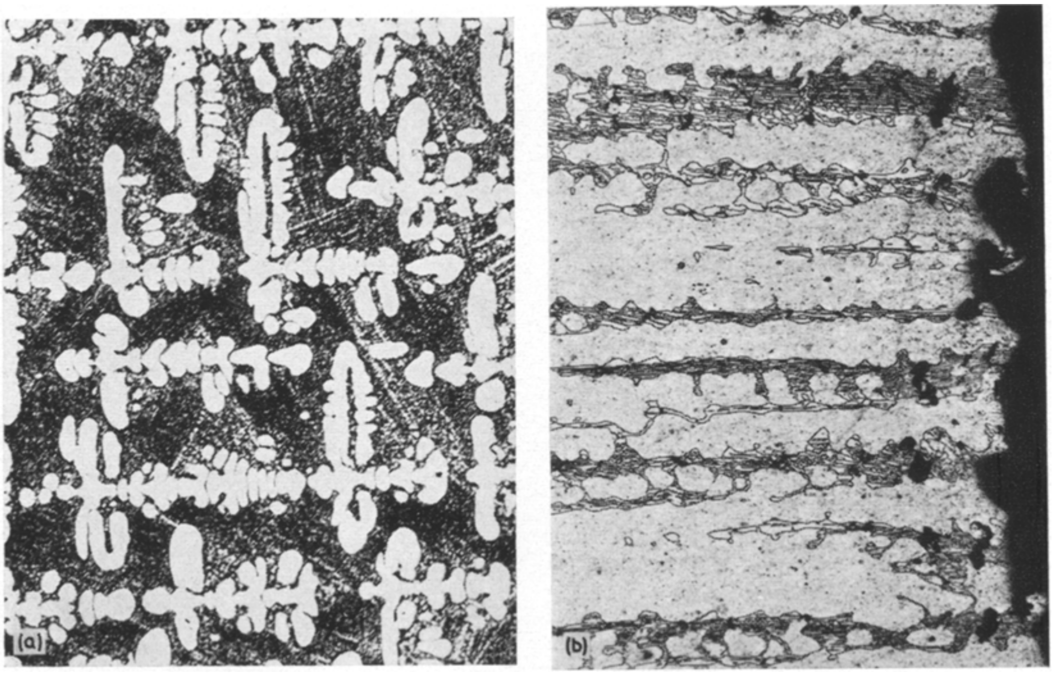

Figure 5 Unetched microsections of hypo-eutectic samples. (a) Transverse section behind a fracture surface in an alloy containing an estimated 56 vol% eutectic (× 134). (b) Longitudinal section of a fracture surface showing the cracking and void formation in the eutectic regions which was confined to the necked portion of the tensile sample. No cracking occurred in the rest of the gauge length (× 173).

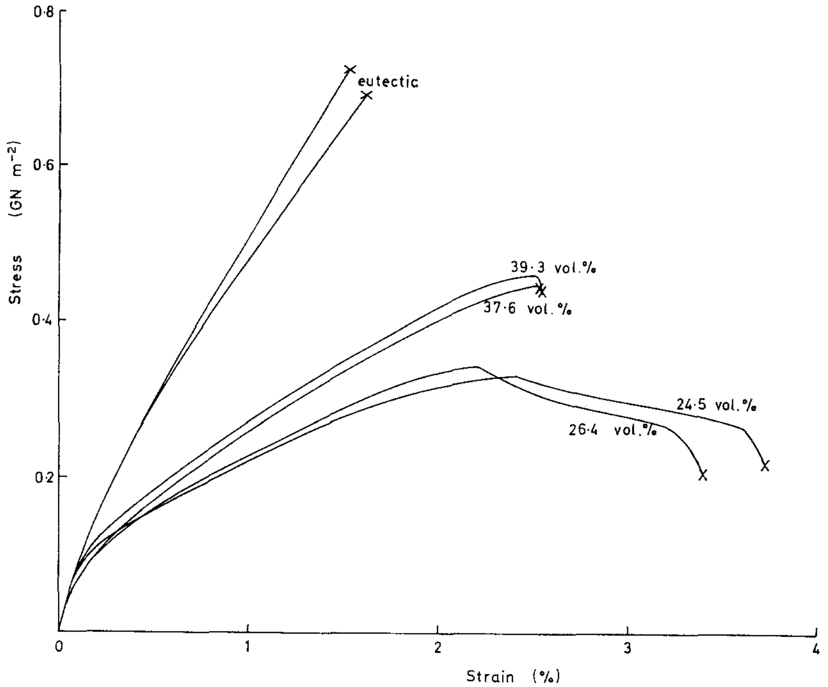

Figure 6 Tensile curves of hypo-eutectic alloys containing various volume fractions of eutectic, showing the increase in total elongation and the occurrence of a mechanical instability at strains beyond the fracture strain of the simple eutectic samples.

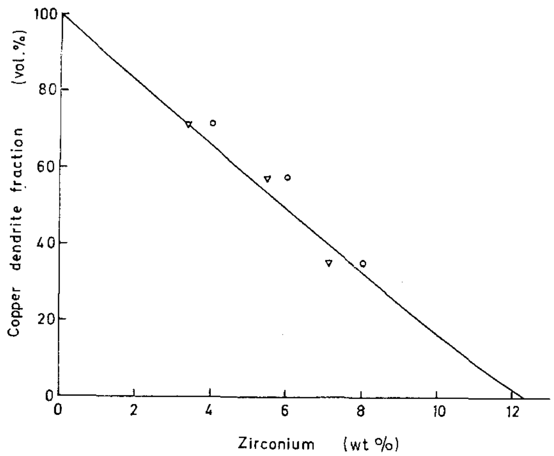

Figure 7 The volume fraction of dendritic copper as a function of the zirconium content of alloys, calculated assuming the density of the Cu_5Zr phase given in the text. The round symbols show the fraction of copper estimated in directionally-grown samples of given zirconium contents and the triangular symbols show the chemical analysis of the same samples. The loss of zirconium during directional solidification is due to a zone-refining effect.

out, leaving samples which are thereby richer in the higher melting point dendritic copper.

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