JOURNAL OF MATERIALS SCIENCE 17 (1982) 3204–3210

On the presence of voids in bronze-route multi-filamentary Nb_3Sn superconducting wires

S. NOURBAKHSH, Y. S. HASCICEK, M. J. GORINGE, J. W. MARTIN
Department of Metallurgy and Science of Materials, University of Oxford, Parks Road, Oxford, UK

The presence of Kirkendall voids in multifilamentary Nb_3Sn superconducting wires prepared by the "bronze-route" has been thought to have an adverse effect on the ductility of the wires. The shape, density and nucleation sites of such voids in commercial Nb/Cu–Sn wires and wires of similar geometry but different scale have been investigated both experimentally and theoretically. The implications of the results for the mechanical properties are discussed.

1. Introduction

Commercial multi-filamentary Nb/Cu–Sn wires in the unreacted form are quite ductile. However, upon full reaction, in the temperature range of 650 to 800° C, to form the superconducting compound Nb_3Sn by the solid state diffusion of Sn into the Nb filaments, the wire loses its ductility to such an extent that it cannot tolerate the stresses during subsequent handling. Microstructural observations of the reacted wires reveal that the transformation of Nb into Nb_3Sn is accompanied by the nucleation and subsequent growth of small voids in the bronze matrix. It has been suggested that these diffusion-related voids are to some extent reponsible for the brittleness of the reacted wire [1, 2]. The aim of the present work is to investigate the mechanisms by which voids form, their possible nucleation sites and their effect on the fracture mechanisms of the reacted wires.

2. Experimental procedure

Two types of wire were examined during this research. They will be referred to according to the number of filaments in the final products. (a) 37 filament wire–37 Nb filaments in 7.2 at% tin bronze matrix; and (b) 5143 filament wire produced from 139 wires similar to (a) but containing also 6 sheathed copper conductors, all encased in a tube of 8 at% Sn bronze. The wires were supplied by AERE Harwell [3].

Short lengths of wire were inserted in alumina tubes having a bore diameter slightly larger than the wire diameter, in order to keep the wire straight and to facilitate the handling of wires after reaction. Wires were then encapsulated in quartz tubing and reacted at various temperatures and times under atmospheric pressure argon, to form Nb_3Sn. They were subsequently bent around drums of various diameters. Optical and scanning electron microscope techniques were used to measure the thickness of the Nb_3Sn layer, the density and distribution of Kirkendall voids, and the distribution and morphology of cracks along the lengths of the Nb core and Nb_3Sn layer.

In order to eliminate the Kirkendall voids a few partially or fully reacted wires were further reacted for two hours at a temperature of 750° C under 15 000 p.s.i.* argon pressure, or a few of the unreacted wires were reacted for 3 days at 780° C under 3000 p.s.i. argon pressure. In both cases the pressure was adequate to eliminate the voids totally.

*1 p.s.i. ~ 6.89 kPa.

0022–2461/82/113204–07$03.34/0

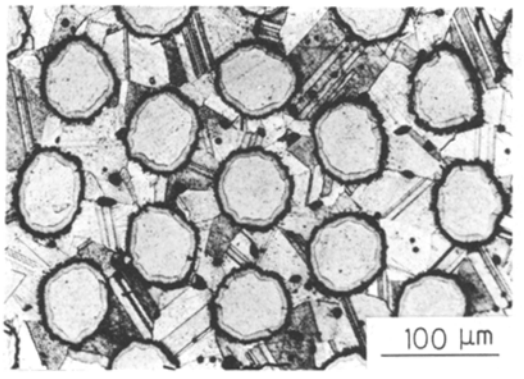

Figure 1 The central area of 37 filament wire reacted for three days at 780° C; cross-section.

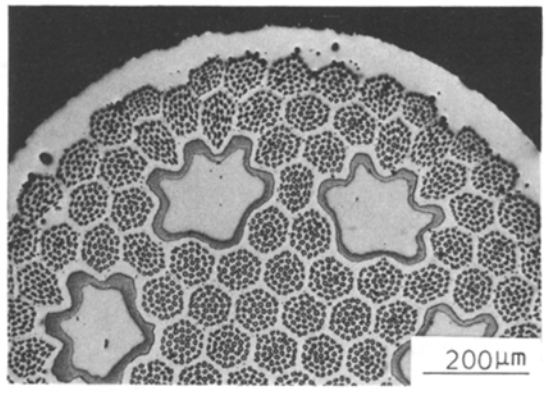

Figure 3 5143 filament wire reacted for three days at 750° C; cross-section.

3. Experimental results

Figures 1 and 2 show the structure of a partially reacted 37 filament wire after 3 days reaction at 780° C under atmospheric and 3000 p.s.i. argon pressure respectively. No change in the growth rate of the layer due to reaction under high pressure was observed. Reaction under high pressure does however produce a more uniform layer growth. In the 37 filament wire, where the interfilamentary spacing is large, Kirkendall voids were mainly observed to be at the grain boundaries.

The density of Kirkendall voids was observed to be much lower in the 5143 filament wire, as was also the volume fraction of voids after the same amount of reaction. In the 5143 filament wire, which has a much finer microstructure ($\sim 1.5\,\mu m$ interfilamentary spacing), the voids occupied the whole space between two or three filaments, during reaction. In this wire, apart from these voids, there were smaller voids also on the grain boundaries of the bronze matrix, delineating the boundaries between the hexagonal units (37 filament) constituting the microstructure. Figure 3 shows the structure of a fully reacted 5143 filament wire.

Figures 4 and 5 show the structure of 5143 filament wire after 3 days reaction at 780° C under 3000 p.s.i. argon. Figures 6 and 7 show the structure of partially reacted 37 and 5143 filament wire respectively after bending. No difference in the behaviour of the two wires was observed. The distribution of cracks was found to be uniform in both wires. Figure 8 shows the structure of a 37 filament wire partially reacted under 3000 p.s.i. pressure after subsequent bending. The structure is similar to that of Fig. 6 indicating that Kirkendall voids have no apparent effect on the distribution of cracks. Figure 9 shows the structure of a 5143 filament wire fully reacted (under 3000 p.s.i. argon) and slightly bent. Deformation and cracking is concentrated in narrow regions. The wire was extremely brittle. The same behaviour was

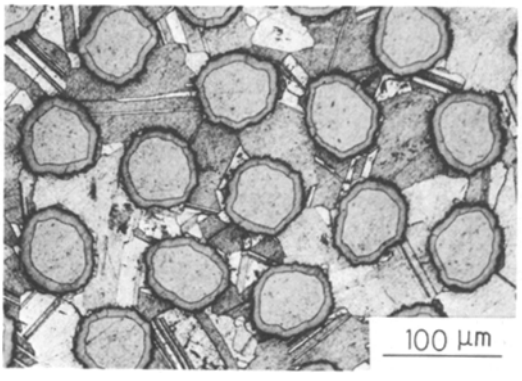

Figure 2 The central area of 37 filament wire reacted under 3000 p.s.i. argon pressure for three days at 780° C; cross-section.

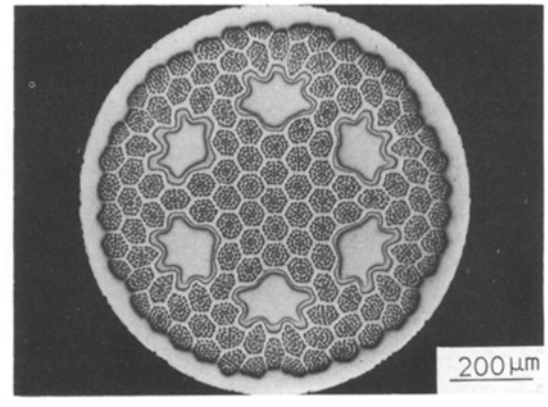

Figure 4 5143 filament wire reacted for three days at 780° C under 3000 p.s.i. argon pressure; cross-section.

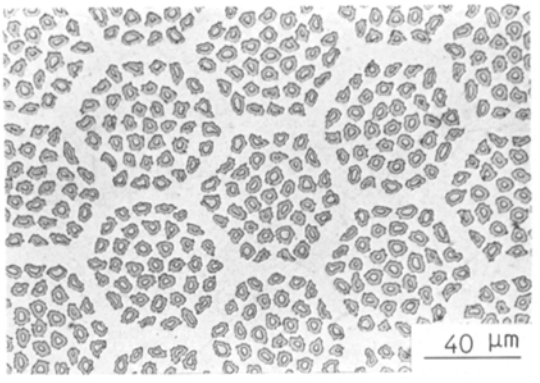

Figure 5 Central area of 5143 filament wire reacted for three days at 780° C under 3000 p.s.i. argon pressure; cross-section.

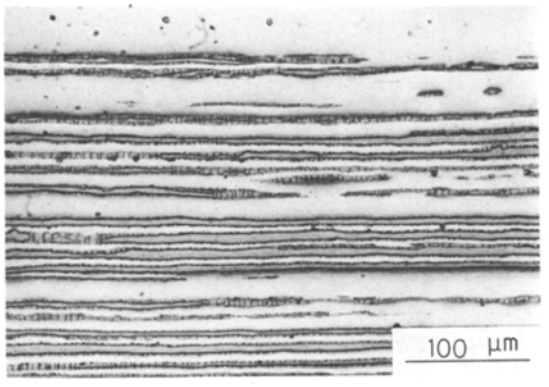

Figure 7 5143 filament wire reacted for six hours at 700° C and bent; longitudinal section.

observed when voids were present. A few fully reacted 5143 filament wires were drawn by 10%. The deformed wires were found to be rather ductile. Figure 10 shows the structure of the wire after drawing.

4. Discussion

Voids which form in the diffusion zones of diffusion couples prepared from two different metals with a substantial difference in interdiffusion rates, are known as Kirkendall voids. The existence of such voids was first reported by Smigelskas and Kirkendall [4]. The following mechanisms have been proposed as being responsible for void formation.

(1) Generation of an excess concentration of vacancies, about 100% above the equilibrium value, resulting from unequal diffusion of atoms across the interface. Voids are formed subsequently by the homogeneous precipitation of these excess vacancies [5].

(2) Generation of an excess concentration of vacancies, about 1.1% above the equilibrium value, and their subsequent condensation on heterogeneous sites, e.g. pre-existing voids, inclusions or interfaces, to form voids [5, 6].

(3) The biaxial tensile stresses parallel to the interface generated in the part of the diffusion zone which is losing atoms [7]. In the presence of this stress, voids larger than a critical size will grow by absorbing vacancies when their concentration is maintained at its equilibrium value.

The excess vacancy concentration of 100% required for homogeneous nucleation of voids was thought to be too high to exist and mechanism No. 2 was favoured by a number of investigators. In the second mechanism nuclei of diameter in the order of 300 nm must exist before vacancies can condense and form voids [8]. A relationship in the form of

$$\frac{2\gamma}{R} = knT \ln (C/C_0)$$

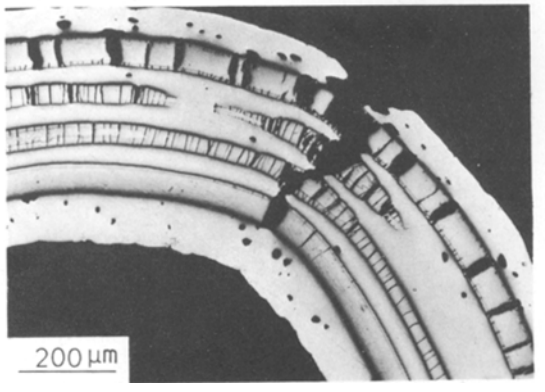

Figure 6 Partially reacted and bent 37 filament wire; longitudinal section.

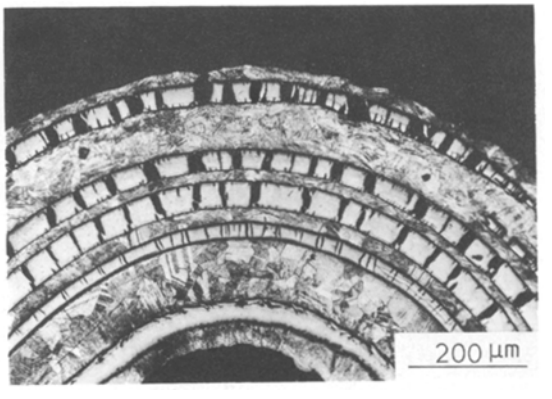

Figure 8 Partially reacted under pressure and bent 37 filament wire; longitudinal section.

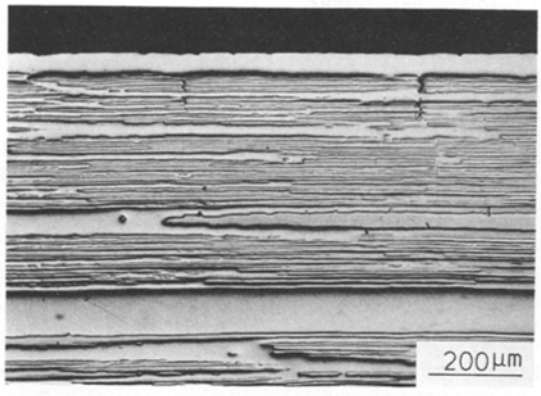

Figure 9 5143 filament wire reacted for 3 days at 780° C under 3000 p.s.i. argon, and slightly bent; longitudinal section.

exists between the radius of nuclei (R) and supersaturation of vacancies C/C_0. k and n are Boltzmann's constant and atomic density respectively.

In the third mechanism, with a relatively small number of annihilated vacancies (C_1) 0.1%, the tensile stresses created are comparable to the yield stress of the material. Voids can nucleate and grow even in the absence of heterogeneous sites and concentration of excess vacancies, according to the relationship [9]

$$\sigma = \frac{2\gamma}{R}, \qquad \sigma = E\sqrt[3]{C_1}.$$

In order to envisage the possible mechanism responsible for the formation of voids in multifilamentary superconducting wire, the following isotropic model is assumed – see Fig. 11.

(1) The wire consists of an array of hexagonal units of Cu–Sn matrix with a central cylindrical core of Nb in each unit.

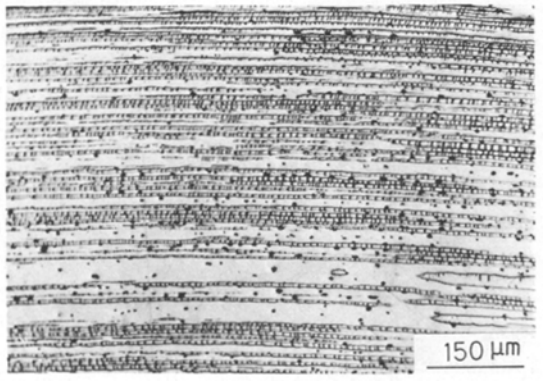

Figure 10 5143 filament wire reacted for three days at 700° C and drawn 10%; longitudinal section.

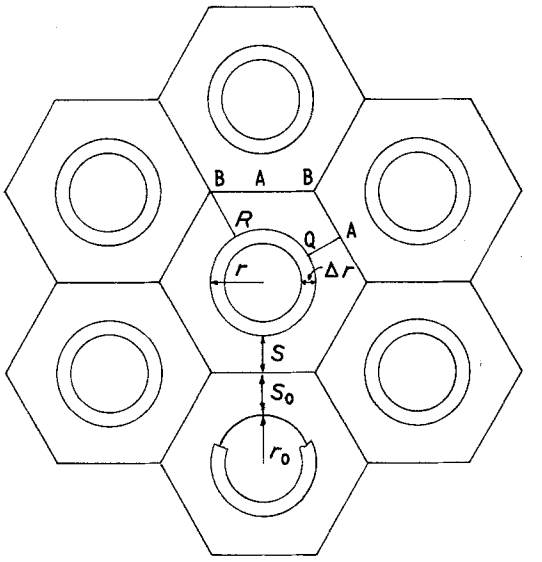

Figure 11 The model on which the calculation is based.

(2) The length of the wire is substantially larger than its diameter.

(3) The length of the wire remains unchanged during reaction.

(4) The lattice parameter of the matrix is independent of Sn concentration.

(5) The diffusion rate of Nb into bronze is taken to be zero.

Calculations (see Appendix) indicate that mass transport of Cu atoms from the region between two (position A – see Fig. 11) into regions between three filaments (position B) is required in order to relax the tangential stress fields set up during reaction, if no Kirkendall voids are allowed to form. The diameter of the wire also increases as a result of total volume expansion of the components. If no mass transport of Cu atoms is allowed, then the volume of voids needed to relax the tensile stress field would be larger than the net volume of Sn atoms which have crossed the Nb_3Sn–Cu interface during reaction.

The voids should nucleate either in positions A where tensile stresses are the largest or in positions B where the expansion of volume is taking place, if their formation is going to be effective in reducing the strain field. Voids nucleated in position A should have an elongated shape with their longer axes lying normal to the filament. Voids nucleated in positions B should be equiaxed. The optical metallography results from the partially reacted 37 filament wire indeed

indicate the existence of such voids (Fig. 1). The radial stress field in the bronze in the area between two filaments is either zero or compressive, and contact between the filaments and the matrix is maintained during reaction. The matrix in the area between three filaments is under tension. The more-or-less uniform layer growth indicates that voids rarely form at the interface, though Sn atom-vacancy exchange actually takes place there. Voids which do form parallel to the interface contribute little to the stress relaxation and inevitably increase the total density of voids.

Now, if mass transport of Cu atoms is taken into account, then the void density should decrease with decrease in the scale of the microstructure (shorter diffusion distance). The experimental results clearly indicate that the void density is indeed much lower in 5143 filament wire than 37 filament wire. The model also indicates that the void density should be lower in wires externally reacted (e.g., by coating with a layer of tin) than in the present internally reacted wires. This is because shrinkage of the matrix does not take place in the "external" case, but it expands due to an excess diffusion of Sn into Cu and into the area under tension. Results obtained by Cogan *et al.* [10] indicate that the density of voids is lower in the area between the filaments in the wires produced by external diffusion. The effect of hydrostatic pressure would be either to counteract the tensile stresses and therefore prevent void formation or, if voids are already present, i.e., in reacted wires, to force them to collapse through the diffusion of vacancies from them to appropriate sinks. During reaction the Nb_3Sn layer is constantly under tension. The amount of tangential tensile strain in any point in the layer is

$$e = \frac{K}{\left[1 + \left(1 - \frac{\Delta r}{r}\right)^2 (K^2 - 1)\right]^{1/2}} - 1,$$

where Δr and r are the distances from the point of interest to the Nb_3Sn–Nb interface and the centre of the filament respectively. After full reaction, every point in the Nb_3Sn filament will experience a tensile strain of $e = K - 1$, where K is the radial expansion of filament, which is about 17% $\{K = [(a^3 Nb_3Sn)/(3a^3 Nb)]^{1/2} = 1.166\}$. No radial cracking is observed to the extent which is needed to relieve the tangential stress field in the filament, and this suggest that outward diffusion of Nb atoms, possible through the cracks, is occurring during reaction.

During tensile straining, the stress acting on the reacted layer continuously increases and eventually reaches a critical value corresponding to the fracture stress of the brittle layer. A single crack in the form of a hoop forms in the layer, and the stress in the immediate vicinity of it in the layer drops to zero [11]. The stress in the layer increases with distance from the crack. Upon further straining, at a distance far away from the first, the stress reaches the fracture stress again and a second crack forms [11]. Therefore cracks tend to distribute themselves uniformly along the length of the filament. The Nb core behaves in a similar manner, but since the fracture stress is higher for Nb, the crack separation would be larger. The wire continues to deform by multiple cracking of the Nb_3Sn layer, plastic deformation and multiple cracking of the Nb core and plastic deformation of the bronze matrix to a rather large strain ~ 10%. This mode of deformation occurs in the partially reacted wires, where the volume fraction of Nb_3Sn is small.

When the crack size is comparable to the interfilamentary spacing, i.e., in the fully reacted wires, then the stress at the head of the crack causes nearby filaments to crack. Cracking spreads sideways and deformation will be concentrated in narrow regions normal to the wire axis. Consequently the wire fails shortly after the first crack forms in the brittle filaments. In the fully reacted and subsequently drawn wire, though the filaments are extensively cracked, the wire is noticeably less brittle than the wire in which the filaments are not precracked. This is because the cracks distribute the strain uniformly in the bronze matrix along the length of the wire.

No change in the distribution or the density of cracks and crack opening was observed as a result of void elimination. This is in disagreement with the work of Easton and Kroeger [1] and West and Rawlings [2] who postulated that void elimination should increase the ductility of wire. Small voids can not only initiate cracks, but also act as crack stoppers [12]. A uniform distribution of very small voids is likely to increase the ductility of the fully reacted wire, by forcing the filaments to crack uniformly along the length of the wire.

Since the size of voids is large and they are elongated parallel to the wire axis, their influence on the initiation of cracks should be negligible in

comparison with the surface irregularities of the filaments.

5. Conclusions

(1) The tangential stress fields created in the bronze matrix during reaction are likely to be responsible for Kirkendall void formation.

(2) Grain boundaries are the main nucleation sites for void formation. The void shape depends upon its position in the structure. There is a close agreement between the predicted and the observed shape of voids.

(3) In partially reacted wires, where the volume fraction of Nb_3Sn is low, filaments deform and crack independently of each other. Both the Nb core and the Nb_3Sn layer crack, but the crack separation is different. Deformation along the wire is uniform and the wire is ductile.

(4) In fully reacted wires, fracture of a filament causes nearby filaments to crack. Deformation is inhomogeneous, and the wire fails at low strains.

(5) Voids have no apparent effect either on the crack initiation or the distribution of cracks in the Nb_3Sn layer. The ductility of the wire remains unchanged in the absence of voids.

Acknowledgements

The authors wish to thank Dr J. Lee and his colleagues at AERE Harwell for kindly providing the wires used in the investigation and for helpful discussions, and Professor Sir Peter Hirsch for provision of laboratory facilities and encouragement. Financial support from the Turkish Ministry of National Education (YSH) and SERC is gratefully acknowledged.

Appendix: Calculation of void densities

In the hexagonal array of filaments (Fig. 11) consider unit length. For the initial unreacted filament let r_0 be the radius of niobium and S_0 be the distance to the flat face of the hexagonal unit. After a certain amount of reaction let

r = outer radius of filament

Δr = layer thickness of Nb_3Sn

S = distance to the face of the hexagon.

Setting $V_{Nb'}$ as the volume of niobium which has undergone reaction and K as the linear expansion ratio between reacted (Nb_3Sn) and unreacted (Nb) material (length of filament assumed fixed) we may write

$$K = (a^3_{Nb_3Sn}/3a^3_{Nb})^{1/2} \quad \text{(A1)}$$

and

$$V_{Nb'} = \frac{\pi(r^2 - (r-\Delta r)^2)}{K^2}, \quad \text{(A2)}$$

where $a_{Nb_3Sn} = 0.528\,\text{nm}$ and $a_{Nb} = 0.33\,\text{nm}$ are the unit cell dimensions of the cubic structures of Nb_3Sn (A15) and Nb (A2) respectively.

The number of Sn atoms which have diffused into the layer is

$$N_{Sn'} = \frac{2V_{Nb'}}{3a^3_{Nb}} = \frac{2\pi[r^2 - (r-\Delta r)^2]}{3K^2 a^3_{Nb}}, \quad \text{(A3)}$$

and is equal to the number of Sn atoms removed from the matrix. The volume shrinkage of the bronze matrix because of this loss of Sn atoms is given by the factor k^3

$$k^3 = 1 - \frac{N_{Sn'}a^3_{br}}{4V_{br}} = 1 - \frac{V_{Nb'}a^3_{br}}{6V_{br}a^3_{Nb}}, \quad \text{(A4)}$$

where $a_{br} = 0.36\,\text{nm}$ is the cubic cell (A1) side of the bronze (assumed constant) and V_{br} is the initial volume of bronze.

Three possible approximations are worthy of consideration:

(1) If plastic deformation of the matrix and mass transport of Cu atoms are both ignored, then the volume fraction of *geometrically necessary* voids is given by

$$f_1 = \frac{3(S_0k + r)^2 - \pi r^2 \sin 60}{[3(r_0 + S_0)^2 - \pi r_0^2 \sin 60]k^3} - 1, \quad \text{(A5)}$$

where the observed radius, r, and the initial radius, r_0, of the filaments are related by

$$r_0K = r[1 + (1 - \Delta r/r)^2(K^2 - 1)]^{1/2}, \quad \text{(A6)}$$

(2) If all the vacancies generated at the Nb_3Sn-bronze interface condense to form voids, then the volume fraction of these voids in the matrix would be

$$f_2 = \frac{1-k^3}{k^3}. \quad \text{(A7)}$$

(3) If the matrix is allowed to deform plastically to some extent then the radial distance between the corners of the hexagon and the filament surface (e.g. BR in Fig. 11) should vary with k during reaction, since the cross-section of the matrix here is larger than that directly between filament pairs (e.g. AQ). The volume fraction of voids in this situation becomes

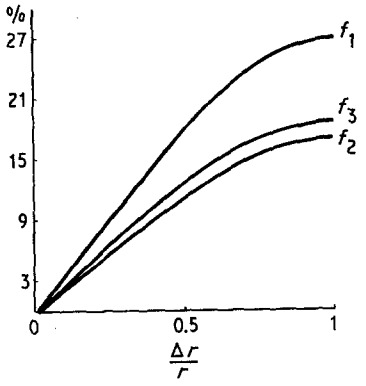

Figure 12 Curves showing variation of the volume fraction of voids in the matrix under the conditions defined for Equations (A5), (A7) and (A8), as a function of extent of reaction (measured by $\Delta r/r$). Initial condition $S = r_0/2$.

$$f_3 = \frac{3\{[(S_0 + r) - r_0 \sin 60]k + r \sin 60\}^2 - \pi r^2 \sin 60}{[3(r_0 + S_0)^2 - \pi r_0^2 \sin 60]k^3} - 1. \quad \text{(A8)}$$

Typical curves for f_1, f_2, f_3 as a function of degree of reaction ($\Delta r/r$) are plotted in Fig. 12. In general $f_1 > f_3 > f_2$. In all cases the regions between filament pairs (A in Fig. 11) are under tangential tensile stress. Voids forming there should be elongated towards the centre of the filaments. The regions mid-way between three filaments (B) are under more or less hydrostatic tensile stress – voids forming there should be equiaxed. If short-range transport of Cu atoms occurs then the voids will tend to become spherodized. Before that happens, however, voids in positions A take on an oval shape with their centres equidistant from the two filaments.

When void formation is suppressed (e.g. during HIPPing) the distance $2S$, between the surfaces of filament pairs decreases during reaction according to

$$S = \left\{ \left[(S_0 + r_0)^2 k^3 + \frac{\pi}{3}(r^2 - r_0^2 k^3) \sin 60 \right]^{1/2} - r \right\}. \quad \text{(A9)}$$

References

1. D. S. EASTON and D. M. KROEGER, *IEEE Trans. Mag.* MAG-15 (1979) 178.
2. A. W. WEST and R. D. RAWLINGS, *J. Mater. Sci.* 14 (1979) 1179.
3. J. A. LEE, C. F. OLD and D. C. LARBALESTIER, CNRS, International Colloquium, No. 242, "Physique sous champs Magnetiques Intenses" (CNRS, Paris, 1975) p. 87
4. A. D. SMIGELSKAS and E. O. KIRKENDALL, *Trans. Amer. Inst. Min. Met. Eng.* 171 (1947) 130.
5. F. SEITZ, *Acta. Met.* 1 (1953) 355.
6. R. W. BALLUFFI, *ibid.* 2 (1954) 194.
7. J. A. BRINKMAN, *ibid.* 3 (1955) 140.
8. R. S. BARNES and D. J. MAZEY, *ibid.* 6 (1958) 1.
9. F. ALDINGER, *ibid.* 22 (1974) 923.
10. S. F. COGAN, D. S. HOLMES and R. M. ROSE, *Appl. Phys. Lett.* 35 (1979) 557.
11. S. OCHIAI and Y. MURAKAMI, *Metal. Sci.* 10 (1976) 401.
12. D. R. BISWAS, *J. Mater. Sci.* 16 (1981) 2434.

Received 3 March
and accepted 22 March 1982