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Superconducting properties of the composite-processed Nb_3Sn superconductor with the Cu-Sn-Zn matrix

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Effects of the Zn addition to the Cu–Sn matrix of the Nb_3Sn composite tape have been investigated by measuring the matrix work-hardening behaviour, the rate of Nb_3Sn layer formation and the pertinent superconducting properties. The Zn addition drastically enhances the diffusion rate of Nb_3Sn formation at each Sn level in the matrix examined, leading to sufficient superconducting properties even at a low Sn level of 3.5 at. %; a sample containing 3.5 at. % Sn and 15 at. % Zn in the matrix exhibits a critical temperature and critical current density comparable with those of samples at a Sn level of 7 at. %. The upper critical field obtained for a sample with the 6 at. % Cu–6 at. % Sn–4 at. % Zn matrix beyond 200 kOe. The work-hardening of the composite matrix is found to be essentially a function of Sn level, and insensitive to the Zn addition.

1. Introduction

The difficulty in applying compound superconductors to practical superconducting systems arises from their extreme brittleness, thus having caused the development of various new fabrication processes. From the technological point of view, the so-called composite process [1] may be considered excellent because of its simplicity and potential to produce multifilamentary superconducting wires. In a typical composite process for producing an Nb_3Sn or V_3Ga wire, a composite consisting of an Nb core in a Cu–Sn alloy matrix or a V core in a Cu–Ga alloy matrix is cold-worked into a wire with repeated intermediate anneals, and exposed to subsequent heat treatment usually in the temperature range 700° C to 800° C for Nb_3Sn or 600° C to 700° C for V_3Ga formation. At present, the best superconducting properties commercially attainable are associated with materials from Nb_3Sn or V_3Ga. However, rapid growth of superconductive applications to date urgently demands further progress in superconducting materials. Recently, attempts have been made to improve superconducting properties of composite-processed Nb_3Sn and V_3Ga superconductors by adding a third element to the core or/and the matrix. Zr-doping in the Nb [2] or the V [3] core has been found to refine the compound grains, resulting in remarkable enhancement of the critical current density, J_c. Sn [4] or Zr [2] addition to the Nb core has been reported to increase the growth rate of the Nb_3Sn layer, whereas Al addition reduces the growth rate [5]. According to Weinman *et al.* [6] as well as Howe and Weinman [7], Ga addition to the V core gains substantial improvements in the growth rate and the J_c properties of the V_3Ga layer.

Addition of a third element might be easier to the Cu-base matrix than to the core. Tachikawa *et al.* [8] have shown that the addition of Al to the Cu–Ga alloy matrix promotes the diffusional growth of a V_3Ga layer, causing a considerable increase in critical current, I_c, without appreciable loss in ductility of the composite. Dew-Hughes *et al.* [5] have revealed that the addition of Al both to the Nb core and to the Cu–Sn alloy matrix can raise remarkably J_c of the Nb_3Sn layer at fields up to 80 kOe. Al is known to form a wide range of solid solutions with α-Cu [9], which contributes to the sufficient ductility of Cu–Sn–Al as well as Cu–Ga–Al solid solutions up to appropriate levels

TABLE I The chemical composition of matrix alloys (at.%)

CSZ	Sn	Zn
30	3.5	0
34	3.5	4
38	3.5	8
310	3.5	10
315	3.5	15
50	5	0
54	5	4
58	5	8
60	6	0
64	6	4
70	7	0
74	7	4

of Al content. In this respect, Zn exhibits much more extensive solubility in α-Cu than Al does [10], so that effects similar to those brought about by Al addition might be expected through the Zn addition to the matrix. In the present study Zn was added to the Cu–Sn matrix of the composite-processed Nb_3Sn, and effects of the Zn addition on the Nb_3Sn formation and its superconducting properties were examined.

2. Experimental

The matrix alloys were cast as 15 mm diameter rods and machined to 13 mm diameter. An Nb core was inserted into an axial hole of 6 mm diameter drilled in the rod. Composite tapes with a cross-section of 0.25 mm x 5 mm were then fabricated by cold swaging and rolling with intermediate annealing at 600° C. The nominal compositions of the matrix alloys are shown in Table I.

Specimens cut from the tapes were sealed in silica capsules under an Ar-atmosphere and heat-treated at temperatures between 650° and 850° C for times up to 100 h. Specimen surfaces were then polished carefully and electroplated with Cu on both ends to be used for subsequent measurements. The superconducting critical temperature, T_c, was determined by a standard resistive technique. I_c was measured using a four-probe method in a liquid He bath under a transverse magnetic field of 65 kOe. Measurement of the upper critical field, H_{c2}, was performed for some selected samples at the Francis Bitter National Magnet Laboratory.

After the I_c experiment, the cross-section of each sample was examined metallographically. The reacted layer thickness, d, was measured, which in turn was used for the calculation of J_c, The composition profile of the layers was inspected by electron-beam microprobe analysis. Fracture appearance of selected samples was examined by means of a scanning electron microscope to monitor the grain size of the Nb_3Sn layers.

3. Result and Discussion

3.1. Ductility of matrix alloys

The ductility of matrix alloys was evaluated on the basis of a Vickers hardness measurement. An available Cu–Sn–Zn phase diagram [11], where the

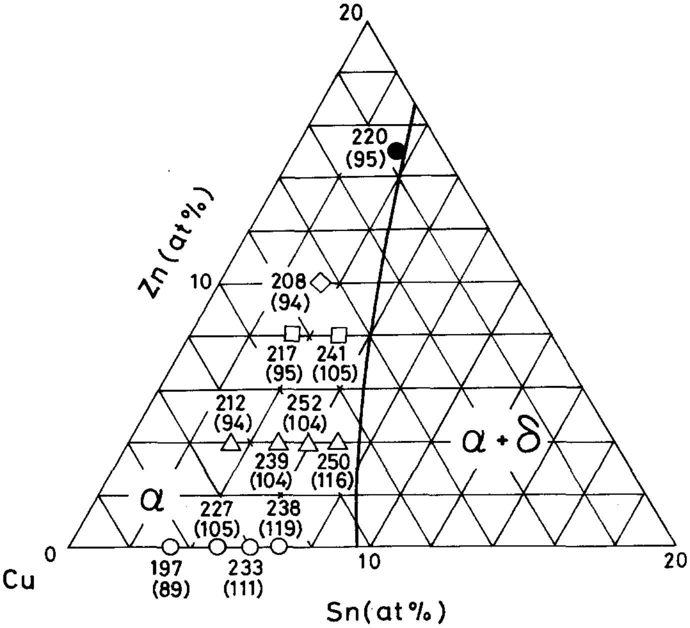

Figure 1 Isothermal section of the Cu–Sn–Zn phase at 500° C [11]. Numbers assigned to each mark of the matrix compositions with and without a bracket indicate Vickers hardness values for as-annealed and 50% cold-worked states, respectively.

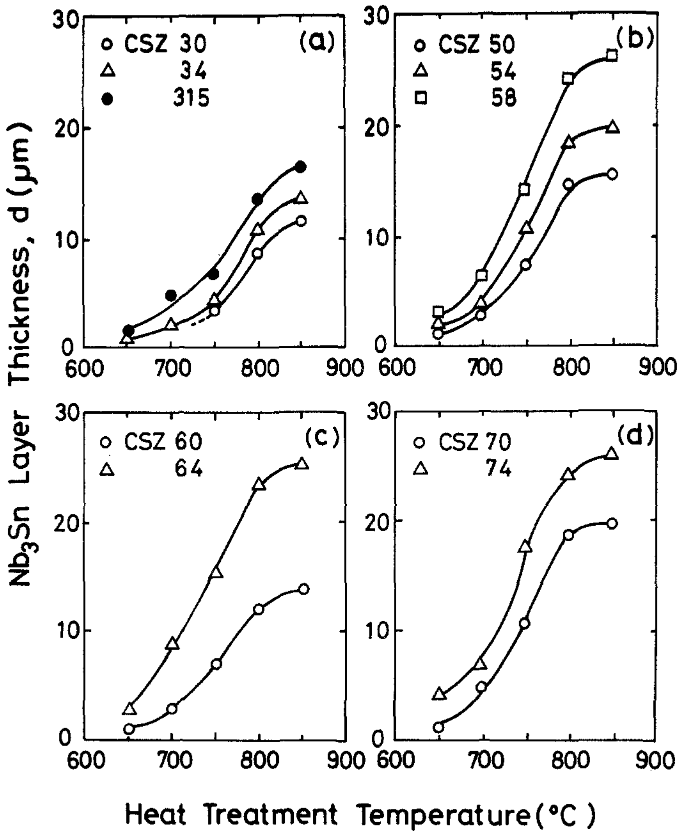

Figure 2 Nb_3Sn reacted layer thickness as a function of heat treatment temperature, heating period being 100 h.

compositions of the present matrix alloys were plotted, Fig. 1, shows that all the compositions are within the α-solid solution range, while some of them, namely CSZ315, CSZ58 and CSZ64, are situated very close to the $\alpha/\alpha + \delta$ phase boundary. At a given Sn level, increasing Zn content causes a slight increase in hardness for the 50% cold-worked state, as indicated in Fig. 1. However, the work-hardening behaviour of the matrix alloys depends more strongly on the Sn level than on the Zn level. It may be concluded that all the matrix alloys used in the present study have sufficient ductility at room temperature.

3.2. Growth of the reacted layer

The thickness of the reacted Nb_3Sn layer, d, is strongly affected by Zn addition. In Fig. 2a to d, d is plotted versus heating temperature, the heating period being 100 h. For CSZ30 heat-treated at 650° C as well as at 700° C, d was too small to be measured. The Nb_3Sn layer growth rate increases with increasing temperature. Raising the Sn level in the matrix causes an evident increase in the growth rate for each temperature examined. At a given Sn level, the growth rate increases significantly with increasing Zn content. However, the most pronounced effect of the Zn addition on the growth rate is observed for intermediate Sn levels of 5 and 6 at.%. For example, a Zn addition of 15 at.% in CSZ315 causes a smaller increase in d than a Zn addition of 4 at.% in CSZ64 does. Lower d values for CSZ315, compared with those for CSZ64 may be attributed to premature Sn depletion in the matrix.

For a given compostion and heating temperature, a general equation

$$d = At^n$$

is known to hold empirically, where t is the heating period and n and A are constants. In Fig. 3 log d is plotted versus log t for four selected samples heated at 800° C for up to 100 h. n corresponds to the gradient of the straight lines drawn through the points and is found to be consistently around 0.5 for all these compostions. This implies that the Nb_3Sn layer in these specimens is grown through a diffusional process. n values ranging from 0.35 to 1 have been reported on the growth of Nb_3Sn [12], and the origin of different n values has been discussed [5]. But since rather thin reacted layers have been generally used to evaluate n

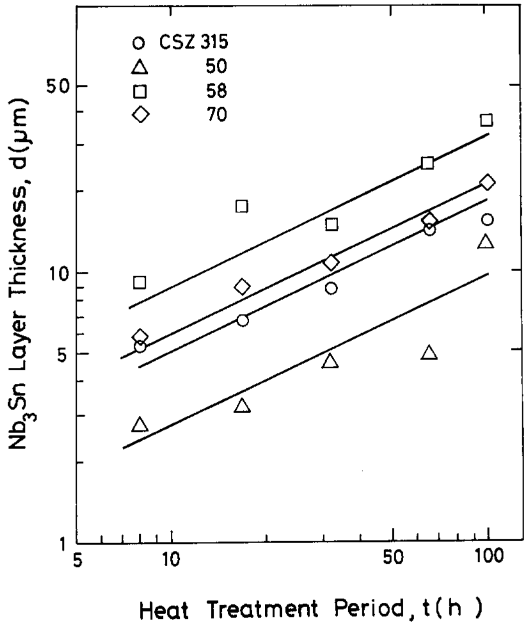

Figure 3 Logarithmic Nb_3Sn layer thickness as a function of logarithmic heat treatment period, heating temperature being 800° C.

values, the irregular nature of the reacted-layer boundaries seems to reduce the reliability of this kind of discussion. In the present study relatively thick layers were the object of examination to avoid ambiguity with d. The constant A is significantly increased by raising the Sn level and also by the Zn addition as seen in Fig. 3.

Microprobe analysis could detect no appreciable amount of Zn in the reacted layer in any of the samples. Dew-Hughes *et al.* [5] have found the presence of Al in the composite-processed Nb_3Sn layer only when the Al was added both to the matrix and to the core, and the absence of Al in the Nb_3Sn layer even when several at.% Al was added to the matrix alone. A consistent explanation of this effect is not given at present.

3.3. Critical temperature and critical field

The superconducting critical temperature, T_c, showed no systematic dependence on the Zn addition in any of the samples but CSZ315. In Figs. 4a to d, T_c is presented as a function of heating temperature, with the heating period being 100 h. T_c increases with increasing temperature and seems to approach a saturation value at each Sn level. Raising the Sn level causes an increase in T_c at each heating temperature, but the Zn addition at any Sn level fails to make an essential increase in T_c. However, a Zn addition of 15 at.% at a Sn level of 3.5 at.% results in quite a large enhancement in T_c for the entire temperature range examined, and the effect is especially prominent at lower heating temperature. T_c values of CSZ315 are higher than those of any other sample at lower heating temperatures, and comparable with those of samples at Sn levels of 6 as well as 7 at.% at higher temperatures. The maximum in T_c reached about 17.6 K in the present study. The lower T_c values

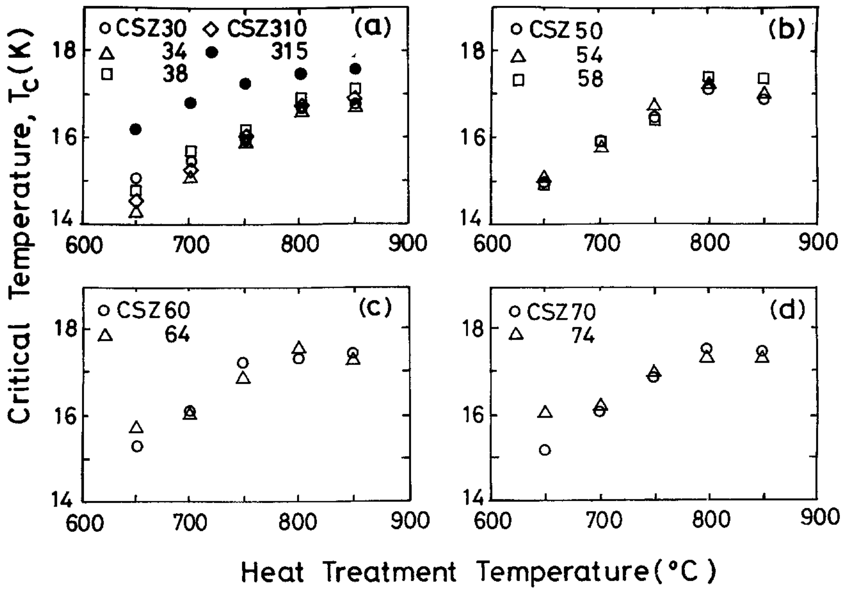

Figure 4 Critical temperature as a function of heat treatment temperature, heating period being 100 h.

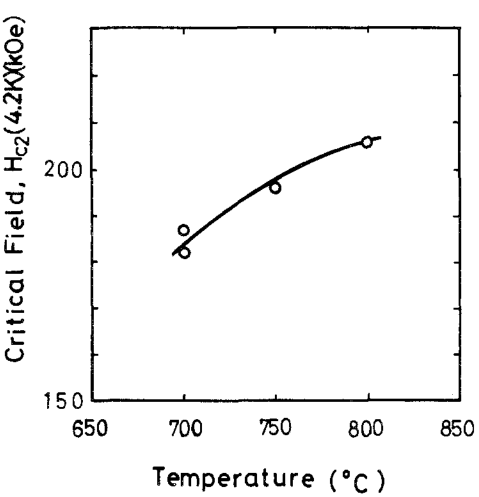

Figure 5 Critical field of CSZ64 as a function of heat treatment temperature, heating period being 100 h.

obtained for lower heating temperatures may be attributed to insufficient integrity of the ordered structure. The general behaviour of T_c in the present study is related to that of d, as pointed out by Luhman and Suenaga [4].

Measurement of the upper critical field, H_{c2}, was performed at 4.2 K on CSZ64 heat-treated at 700°, 750° and 800° C, respectively for 100 h, by means of a standard resistive method. H_{c2} values were determined by extrapolating H versus I_c curves to zero I_c. H_{c2} increases with increasing heat treatment temperature, as shown in Fig. 5. The H_{c2}(4.2 K) value for the 800° C heat-treated specimen is beyond 200 kOe. The general characteristics of H_{c2} with respect to the heating temperature are apparently consistent with those of T_c.

3.4. Critical current and critical current density

The critical current, I_c, was strongly affected by Zn addition. Fig. 6 represents I_c as a function of heating temperature. At each Sn level I_c increases with increasing Zn content. This increase in I_c is primarily due to the increase in d. The effect of the Zn addition is most prominent for intermediate Sn levels of 5 and 6 at.%. A 4 at.% Zn addition at Sn levels of 5 and 6 at.% causes a drastic increase in I_c while at a Sn level of 3.5 at.% more than

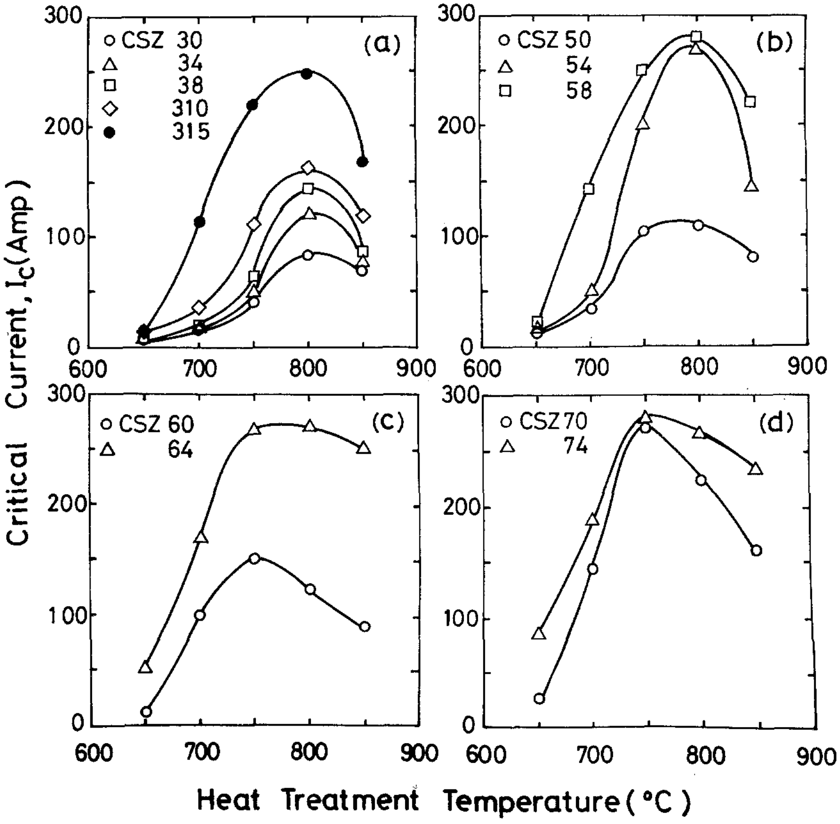

Figure 6 Critical current as a function of heat treatment temperature, heating period being 100 h.

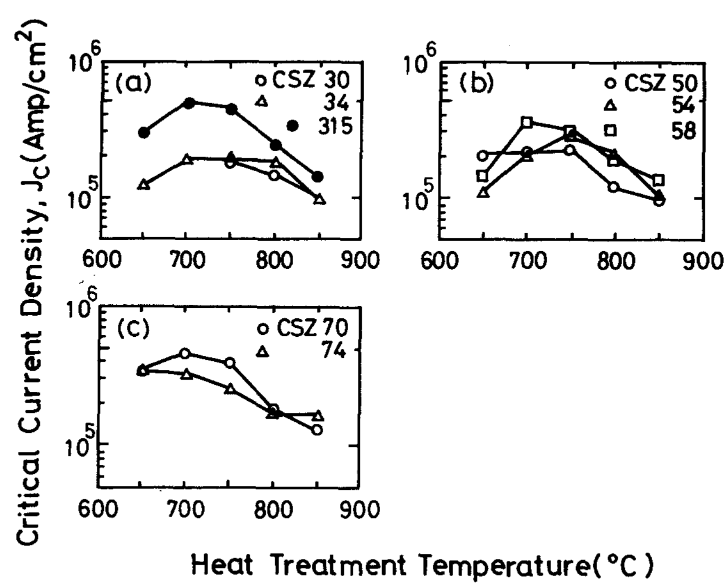

Figure 7 Critical current density as a function of heat treatment temperature, heating period being 100 h.

10 at. % Zn is necessary to gain as much in I_c. Temperatures corresponding to I_c maxima are nearly independent of the Zn addition at any Sn level, and lowered with raising Sn level. The reduction in I_c at higher temperatures is attributed to the reduction of critical current density due to the grain coarsening. As concerns CSZ315, I_c is relatively larger than that expected from its d value and is comparably as high as that of samples at Sn levels of 6 and 7 at.%. In any event, it is feasible to conclude that comparable I_c values are obtained for samples whose matrix composition is situated near the $\alpha/\alpha + \delta$ boundary as denoted in Fig. 1. Similar effects of substitution have been reported on a composite process of the V_3Ga tape where part of Ga in the Cu–Ga matrix is replaced by Al [13].

The critical current density, J_c, ranges between 1 and 6×10^5 A cm^{-2}, as shown in Fig. 7a to c, and increases with increasing Sn level at each heat treatment temperature. J_c was found to be less sensitive to the Zn addition for specimens with the same heat treatment condition, regardless of that for CSZ315. The maximum in J_c seems to appear around 700° C for each sample. At higher temperatures grain coarsening is responsible for the lower J_c values obtained [14]. Fractographs of Fig. 8a to c reveal that grain coarsening of the reacted layers becomes apparent beyond 800° C, consistent with degradation of I_c and J_c as shown in Figs. 6 and 7, respectively. The grain size of CSZ315 heat-treated at 800° C for 100 h is nearly the same as that of CSZ50, as shown in Fig. 8d. The degradation of J_c at 650° C is probably due to insufficient integrity of the reacted layer formed. J_c for CSZ315 is comparably as high as that of CSZ70 at each temperature, which is a rather explicit indication that the reacted layers of both these samples are nearly equal in integrity.

An empirical equation has been found which describes J_c at a given d in the following form [2];

$$J_c(d) = J_c(0) \exp(-nd)$$

where n is the slope of a $\ln J_c(d)$ versus d plot and $J_c(0)$ is the extrapolated zero thickness value of $J_c(d)$ In Fig. 9 $\ln J_c$ is plotted against d regardless of heating temperatures. At each Sn level straight lines can be drawn through the points corresponding to d values for the temperature range where T_c values go to saturation. n seems to be nearly consistent at a given Sn level and decreases with increasing Sn level. Because the grain boundary is a primary pinning centre in the Nb_3Sn superconductor, the slope n is regarded as reflecting the grain-growth behaviour of each sample. The fact that n does not vary with Zn addition is compatible with the observation that Zn is not found in the reacted layer. $J_c(0)$ shows a dependency on the Zn addition, in which $J_c(0)$ increases with increasing Zn content. Since the Zn addition promotes the formation of Nb_3Sn, the time required to grow a given thickness of Nb_3Sn is shortened, and consequently the grain growth of Nb_3Sn might be decreased by the Zn addition. Thus, in the specimens with Zn added the faster growth rate leads to a larger J_c value for a given thickness of Nb_3Sn.

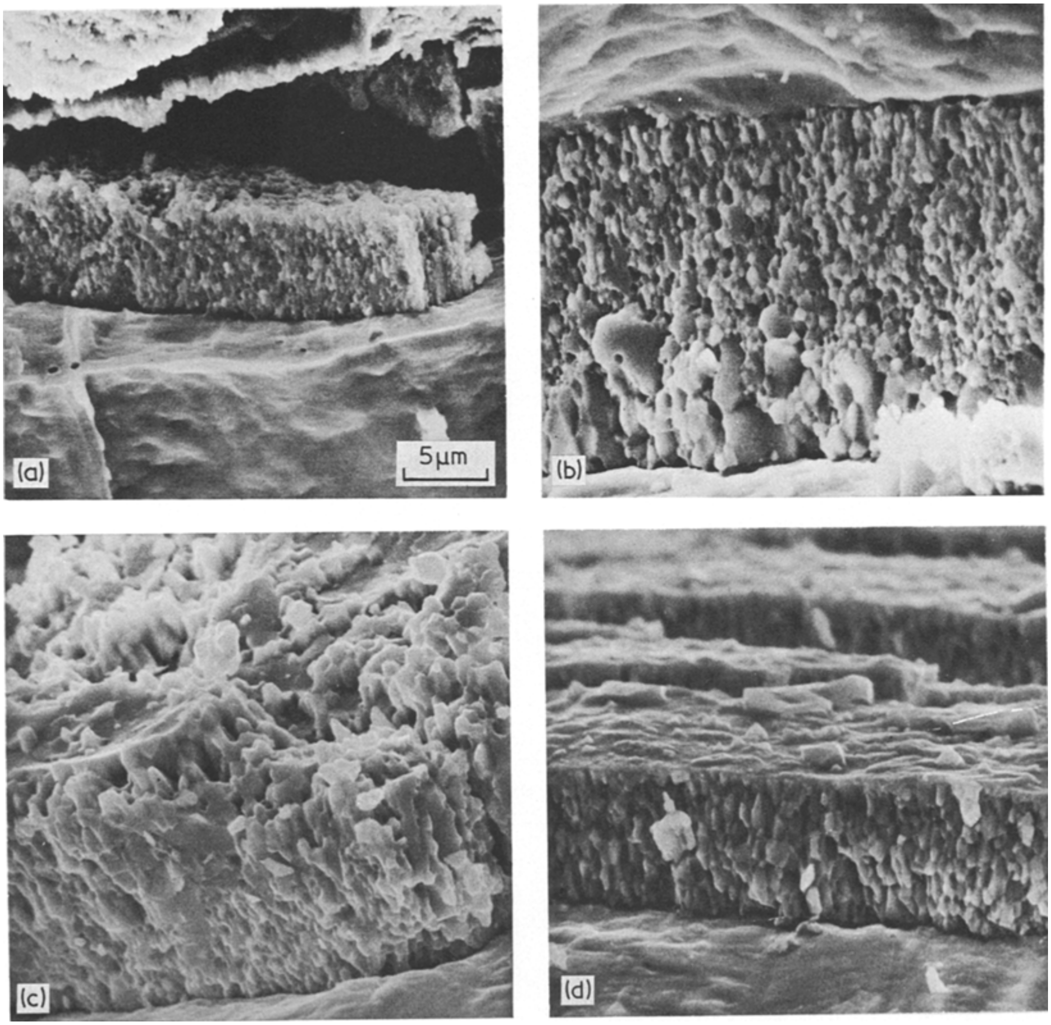

Figure 8 Fracture appearances of composite tapes; (a) CSZ50 heat-treated at 750° C for 100 h, (b) CSZ50 heat-treated at 800° C for 100 h, (c) CSZ50 heat-treated at 850° C for 100 h, (d) CSZ315 heat-treated at 800° C for 100 h.

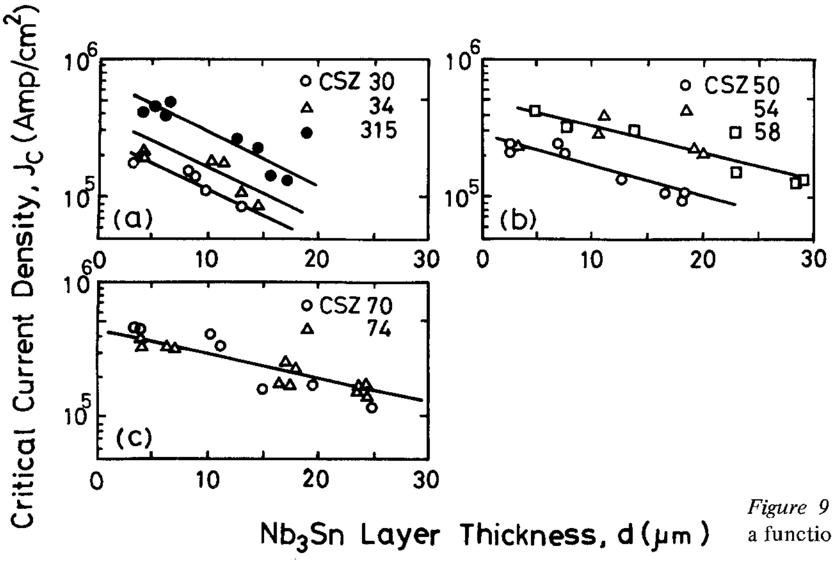

Figure 9 Logarithmic current density as a function of Nb_3Sn layer thickness.

4. Conclusion

In the composite diffusion process of the Nb_3Sn superconductor a substantial part of the Sn in the Cu–Sn matrix can be replaced by a rather large amount of Zn without any essential degradation in the superconducting critical values. The Zn addition causes a marked increase in I_c through increasing the growth rate of the Nb_3Sn layer at each Sn level examined. Excellent I_c properties can be obtained even for samples containing only 3.5 at.% Sn in the matrix which otherwise leads to poor I_c values. The Zn does not dissolve into Nb_3Sn and has no effect on the intrinsic superconducting properties, such as T_c, of Nb_3Sn. However, the Zn may introduce excess vacancies in the Cu–Sn matrix. This increases the supply rate of Sn at the matrix–Nb_3Sn diffusion interface and promotes the formation of an Nb_3Sn layer.

The I_c, J_c and T_c properties of CSZ315 (Cu–3.5 at.% Sn–15 at.% Zn alloy matrix) are comparable with those of samples containing 7 at.% Sn in the matrix. It is inferred that samples with matrix compositions adjacent to the $\alpha/\alpha + \delta$ phase boundary in the Cu–Sn–Zn ternary system (Fig. 1) have approximately the same superconducting properties. A composite process making use of the Cu–Sn–Zn alloy as the matrix may be promising for fabricating the Nb_3Sn multifilamentary wire, since the Zn addition causes an outstanding enhancement in the growth rate of the Nb_3Sn even at low Sn levels without serious loss in the ductility of the composite.

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References

1. K. TACHIKAWA, Proceedings of ICEC-III (Iliffe Science and Technology Publication, 1970) p. 239.
2. M. SUENAGA, T. S. LUHMAN and W. B. SAMPSON, *J. Appl. Phys.* **45** (1974) 4049.
3. Y. FURUTO, T. SUZUKI, K. TACHIKAWA and Y. IWASA. *Appl. Phys. Lett.* **24** (1974) 34.
4. T. S. LUHMAN and M. SUENAGA, *Adv. Cryogenic Eng.* **22** (1976) 536.
5. D. DEW-HUGHES, T. S. LUHMAN and M. SUENAGA *Nuclear Technol.* **29** (1976) 268.
6. L. S. WEINMAN, R. A. MEUSSNER and D. G. HOWE, *Solid State Commun.* **14** (1974) 275.
7. D. G. HOWE and L. S. WEINMAN, *Appl Polymer Symp.* **29** (1976) 25.
8. K. TACHIKAWA, K. ITOH and Y. TANAKA, *IEEE Trans. Mag.* **MAG11** (1975) 240.
9. M. HANSEN, "Constitution of Binary Alloys," (McGraw-Hill, New York, 1958) p. 84.
10. *Idem, ibid* p. 649.
11. Metals Handbook, 8 (1973) p. 431.
12. H. H. FARRELL, G. H. GILMER and M. SUENAGA, *Thin Solid Films* **25** (1975) 253.
13. Y. YOSHIDA, K. TACHIKAWA and Y. IWASA, *Appl. Phys. Lett.* **27** (1975) 632.
14. R. M. SCANLAN, W. A. FIETZ, and E. F. KOCH, *J. Appl. Phys.* **46** (1975) 2244.

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