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Critical current studies on metal clad $R_1Ba_2Cu_3O_{7-x}$ wires

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Abstract. Silver clad wires of $R_1Ba_2Cu_3O_{7-x}$ (R = Y, Gd, Sm, Dy and Ho) have been fabricated following the powder-in-tube method and cold-rolling. The critical current density J_c at 77 K and zero magnetic field is restricted to 66 $A.cm^{-2}$. In a separate experiment we have studied the effect of silver sheath thickness on J_c of the $Y_1Ba_2Cu_3O_{7-x}$ wires. Interestingly, J_c is higher for larger sheath thickness indicating that large sheath thickness prevents oxygen loss during sintering. Uniaxial pressing of the wires into flat tapes results in an increase of the J_c. Maximum J_c is, however, limited to 169 $A.cm^{-2}$. No grain alignment is found in the core material of our wires which is essential for high J_c. Several options are being tried.

Keywords. Critical current; metal clad wires; powder-in-tube method; cold rolling.

1. Introduction

The use of high temperature superconductors is bound to remain severely restricted until they are fabricated into flexible wires or tapes capable of carrying large transport current at 77 K and in the presence of high operating magnetic field. Besides, the fabricated wires/tapes have to possess high yield strength, crushing strength, toughness and fatigue resistance to withstand the electromagnetic forces while in use in devices. Unfortunately all ceramic materials, whether superconducting or not, are characterized by their low strength and toughness and have been used for bulk applications in a limited way. The newly discovered superconductors YBCO, BSCCO and TBSCCO are ceramic in nature and have glass or clay-like layered structure. They can be easily peeled off and thus have poor mechanical properties. Their superconducting properties too are unique and significantly different from the conventional superconductors. For example, these superconductors have large anisotropies of Hc_2 and J_c in a–b plane and along the c-axis (Dinger *et al* 1987; Hagen *et al* 1988; Martin *et al* 1988; Wang and Ong 1988), they are granular in nature with grain boundaries weakly superconducting or non-superconducting (Taylor *et al* 1988). The current transport through grains is assumed to be of Josephson type (Deutscher 1980) which is sensitive to temperature and magnetic field. Yet another problem with these superconductors is the stoichiometric control of a gaseous phase viz oxygen.

The standard method for wire fabrication widely followed is the so-called powder-in-tube method. Silver has been found acceptable as a tube material because of its non-reactivity (Sharma *et al* 1988a) with these superconductors and good permeability to oxygen. This silver cladding provides not only the necessary mechanical strength but also facilitates thermal stabilization (adiabatic, dynamic and cryostatic) required to prevent flux jumps (premature quenching). The early demonstration of $J_c > 10^5$ $A.cm^{-2}$ at 77 K in single crystal of Y_{123} (Dinger *et al* 1987) and in epitaxial Y_{123} films (Chaudhury *et al* 1987) established their potentiality for

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applications. The J_c in bulk polycrystalline materials is, however, limited by low density and random orientation of the grains. Very recently Salama *et al* (1989) have been able to achieve a $J_c = 18500$ a.cm^{-2} at 77 K in Y_{123} with highly-oriented grains obtained by a liquid phase process. Such a method may not be feasible for metal clad wires; nevertheless J_c values as high as 3300 A.cm^{-2} (77 K, OT) in Ag clad tape (Okada *et al* 1988) have been reported. Consistent efforts are therefore being made in overcoming various problems which would lead to the development of these HTSC wires. In this paper we report our studies on J_c of the silver clad wires of 90 K $R_1Ba_2Cu_3O_{7-x}$ superconductors (R = Y, Gd, Sm, Dy and Ho).

2. Experimental

The method of fabrication of Ag-clad wire was described earlier (Sharma *et al* 1988b). Powders of $R_1Ba_2Cu_3O_{7-x}$ (R = Y, Gd, Ho, Dy, Sm) were prepared by the usual solid-state ceramic technique. The twice calcinated powders were sintered in flowing oxygen for 38 h at 940°C, held at 700°C for 5 h, 500°C for 15 h, 450°C for 7 h and finally cooled at 100°C/h to room temperature. Silver tubes (OD 10 mm, ID 6 mm) were then packed with each of the powders and cold-rolled to wires of diameter about 1.1 mm. In a separate experiment Ag-tubes (OD 10 mm, ID 3, 4, 6 and 8 mm) were packed with oxygenated $Y_1Ba_2Cu_3O_{7-x}$ powder at about 10^6 Psi and cold-rolled as usual.

Short specimens of all the composite wires were sintered at temperatures between 800 and 870°C for varying periods under flowing oxygen and cooled at 100°C/h. A four-probe method was used to measure T_c and J_c. A criterion of 1 μV/cm was used to define J_c. XRD was used to check the orthorhombic structure of the oxygenated powders before being used for the fabrication of wires. SEM pictures were obtained on the polished cores of the sintered wires to study the grain morphology.

3. Results and discussion

3.1 $R_1Ba_2Cu_3O_{7-x}$ wires

The measured I–V behaviour of all the wire specimens of Y_{123}, Gd_{123} Sm_{123}, Dy_{123} and Ho_{123} is shown in figure 1. The J_c values of the core materials according to 1 μV/cm are also indicated in the figure. The values of J_c of these wires sintered at different temperatures and for varying periods are listed in table 1. As seen from this table, J_c increases with sintering and annealing duration in all the three Ho_{123}, Sm_{123} and Gd_{123} wire specimens. It is, however, interesting to note that in Ho_{123} specimens J_c increases by a factor of 2 when the second and third reactions are carried out at 855°C whereas in Sm_{123} specimens, where the second reaction is carried out at 550°C only, J_c increases only marginally from 55 A.cm^{-2} to 66 A.cm^{-2}. It thus appears that the sintering of these wires at 830 and 855°C is not complete. It is well known that the sintering temperature required for high density in these superconductors is 950°C (Johnson and Grader 1988). The sintering temperature used in the present study is far below 950°C and thus needs much longer time. The density of the sintered core therefore remains very low $\sim$60–65% of the theoretical value. One problem with Ag-cladding is the low melting point of Ag (940°C in the presence of oxygen). Flukiger *et al* (1988) used 5 at% Pd in Ag as the cladding material which has a slightly higher

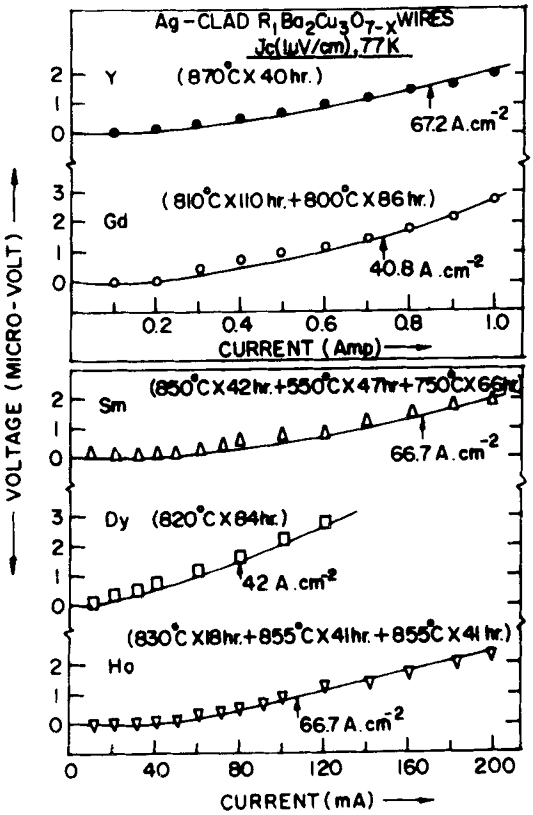

Figure 1. Measured V–I data on Ag-clad wires of $R_1Ba_2Cu_3O_{7-x}$ (R = Y, Gd, Sm, Dy and Ho), J_c values (1 μV/cm) at 77 K are marked by arrows. Sintering temperature and duration are mentioned against each specimens.

Table 1. Sintering parameters and J_c values at 77 K of Ag-clad wires of $R_1Ba_2Cu_3O_{7-x}$ (R = Ho, Dy, Sm, Gd and Y)

Specimen	Sintering temp. & time	J_c(A·cm^{-2})(77 K, OT)
$Ho_1Ba_2Cu_3O_{7-x}$	830°C × 18 h	33.5
	830°C × 18 h + 855°C × 41 h	46.4
	830°C × 18 h + 855°C × 47 h	66.7
$Dy_1Ba_2Cu_3O_{7-x}$	820°C × 84 h	42
$Sm_1Ba_2Cu_3O_{7-x}$	855°C × 18 h	55
	850°C × 42 h + 550°C × 47 h	60
	850°C × 42 h + 550°C × 47 h + 750°C × 66 h	66.7
$Gd_1Ba_2Cu_3O_{7-x}$	810°C × 110 h	33.2
	810°C × 110 h + 800°C × 86 h	40.8
$Y_1Ba_2Cu_3O_{7-x}$	870°C × 40 h	67.2

melting point. The benefit is however too marginal to be of any technological significance. The J_c in all these wire specimens appears to be limited to 66 A.cm^{-2} even though Y_{123} specimen was prepared using John Matthey's five nine purity oxide powders. The low packing density in the starting composite tube and the low sintering temperature perhaps restricts J_c to this low value. Rolling does increase compaction density but not to the desired extent. The reason is that silver is a soft material and does not have enough strength to squeeze and compress the powder. The conductor gets elongated. Press process similar to that used for bulk pellets, on the other hand, increases the density of the core material. Kawashima *et al* (1989) reported enhanced values of J_c in Ag-clad Y_{123} tapes. We have also observed similar behaviour in Y_{123} wires to be described in the next section.

3.2 $Y_1Ba_2Cu_3O_{7-x}$ *wires with different Ag-sheath thickness*

Fresh wire specimens of Ag-clad $Y_1Ba_2Cu_3O_{7-x}$ were prepared using Ag tube of 10 mm OD but different ID viz 3 mm, 4 mm, 6 mm and 8 mm. Packing of the powder in the tubes was carried out at about 10^6 psi. The rolled wires thus had varied Ag-wall thickness. One set of specimens was sintered at 830°C for 38 h and another at 830°C for 38 h followed by another sintering at 810°C for 110 h. The measured I–V behaviour of these specimens are shown in figures 2 and 3 respectively. The sample parameters, sintering details and the measured J_c values (1 μm/cm) are listed in table 2. Specimen Nos 4 and 5, shown as starred, were prepared by pressing wires uniaxially in a die. As seen from table 2, the J_c values increase with decrease in the core dia. In other words, J_c is higher for wires with larger Ag sheath thickness. The same trend is maintained when the specimens are sintered at 810°C further for 110 h except sample No. 3. Probably, the sample was strained during handling. The highest value of $J_c = 169\,A.cm^{-2}$ is obtained for wire with maximum Ag-wall thickness. This is

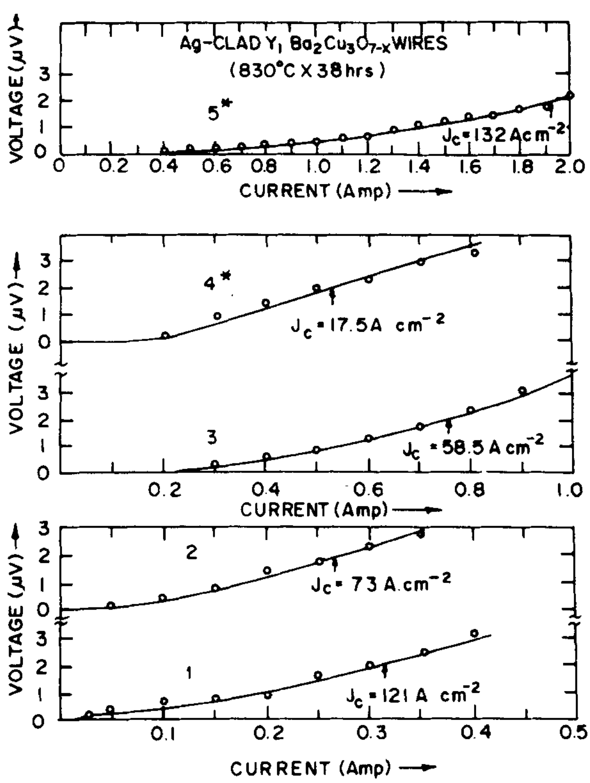

Figure 2. Measured V–I data on Ag-clad $Y_1Ba_2Cu_3O_{7-x}$ wires heat-treated at 830°C for 38 h. Sample parameters are given in table 2. J_c values (1 μV/cm) at 77 K are marked by arrows.

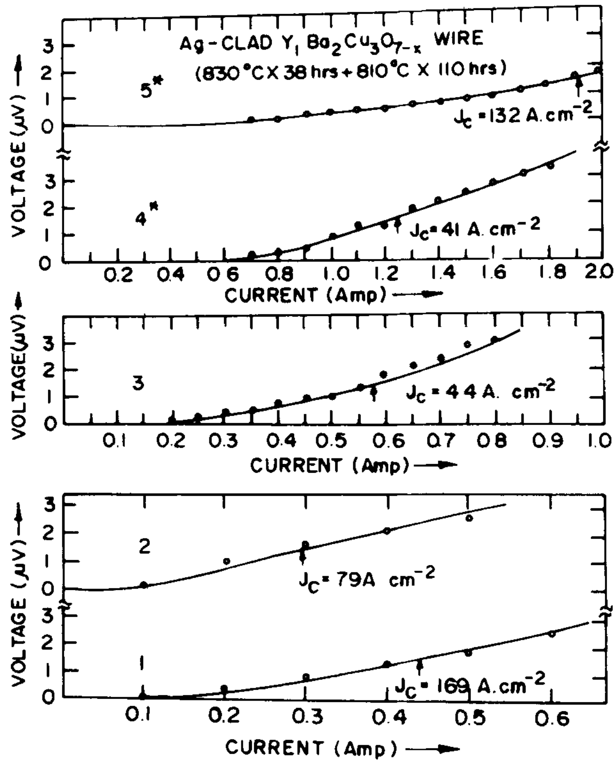

Figure 3. Measured *V–I* data on Ag-clad $Y_1Ba_2Cu_3O_{7-x}$ wires heat-treated at 830°C for 38 h + 810°C for 110 h. Sample parameters are given in table 2. Highest J_c value is obtained for sample no. 1.

Table 2. Dimensions of the Ag-tube, rolled wire and the core, sintering parameters and the J_c values of the $Y_1Ba_2Cu_3O_{7-x}$ wires

Sample No.	Ag-Tube OD (mm)	Ag-Tube ID (mm)	Wire dia (mm)	Core area (cm^2) $\times 10^{-2}$	J_c($A\cdot cm^{-2}$)(77 K, OT) 830°C × 38 h	J_c($A\cdot cm^{-2}$)(77 K, OT) 830°C × 38 h + 810°C × 110 h
1	10	3	1.23	0.26	121	169
2	10	4	1.11	0.37	73	79
3	10	6	1.20	1.30	59	44
4*	10	8	3.50	3.02	18	41
5*	10	4	3.30	1.44	132	132

*Specimen pressed in a die into tapes

contrary to our expectation, since a small Ag-sheath thickness is preferred for oxygen diffusion. In fact higher values of J_c are obtained by partially removing the cladding material (Flukiger 1988) or providing extra channel for O_2 diffusion (Glowacki and Evetts 1987). The preliminary XRD spectra indicate reduced orthorhombicity in wires with smaller Ag-wall thickness which indicates that oxygen stoichiometry is better maintained in wires with thick Ag-sheath. It appears therefore that the loss of oxygen during sintering is prevented by the Ag wall thickness. More detailed XRD spectra

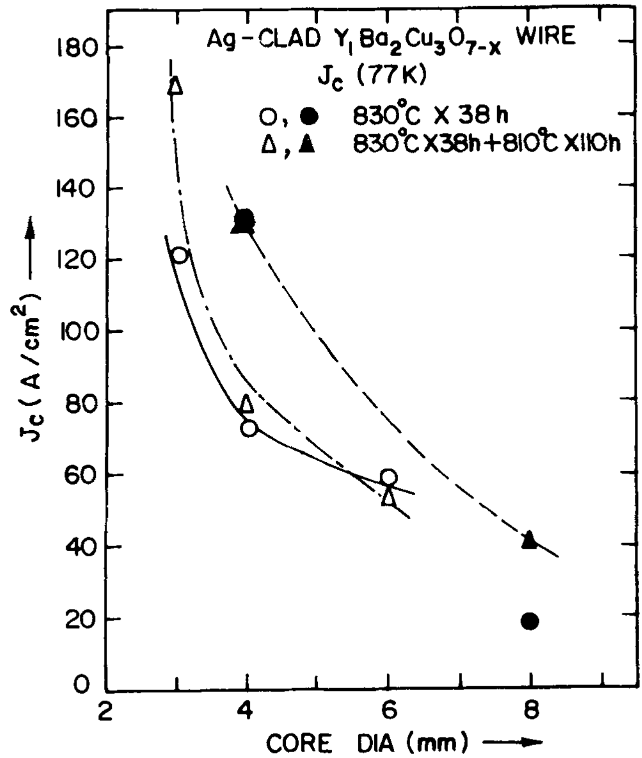

Figure 4. J_c versus core dia. plot of the $Y_1Ba_2Cu_3O_{7-x}$ wire specimens which are detailed in table 2, the filled symbols are for wire specimens which have been pressed at a pressure of 10^6 psi before sintering.

at high resolution will be taken on the core material of these sintered wires. Normal state resistivity of the wire is restored only at a current density of $3500\,A/cm^{-2}$ indicating that grains with this J_c are present in the specimens. The weak links, due to low density, and the random orientation of the grains lead to small value of J_c.

Figure 4 shows the variation of J_c with dia of the core of the starting material for specimen wires of Y_{123} sintered for two durations. The filled symbols represent specimens unaxially pressed to a pressure of 10^6 psi before sintering. Two features are apparent. One that the prolonged sintering is most effective in the specimen with thinnest core, second that the J_c of the pressed samples is higher than the only-rolled wires. Prolonged sintering and higher density obtained by pressing are thus conducive to higher J_c values. More experiments using press technique are in progress.

SEM pictures taken on these sintered cores do not indicate any alignment of grains reported by many workers (see for example Matsumoto *et al* 1989). These authors however have gone to very thin size of tapes, as small as 0.06 mm. In comparison, our specimen sizes are quite large. The J_c value of $169\,A.cm^{-2}$ obtained by us is nevertheless higher than the values obtained by us earlier in this system (Sharma *et al* 1988c). It therefore appears that large Ag-thickness has prevented oxygen loss from the specimen during sintering. The small size of the core could be the other reason for higher J_c as it will provide thermal stability. The increase in J_c compared to the previously studied specimens is thus a combined effect of a higher packing density, thin core and reduced loss of oxygen during sintering.

Apart from the problem of high sintering temperature and aligned grains discussed above a major difficulty faced in wire fabrication is the mismatch of thermal expansion of the ceramic core and the metal sheath. Cracks are developed (Sharma *et al* 1988c; Kohno *et al* 1988) during sintering of the wire due to the tensile stress developed at the interface (caused by this thermal mismatch). Metallization of the core material with 3 wt% Ag metal (Imanaka *et al* 1989) has been reported beneficial for increasing J_c. Our own studies (unpublished) with large Ag addition (20 at%) showed decrease of J_c in wires. Perhaps a small quantity of Ag fills up the pores and improves thermal mismatch of the core with the Ag sheath whereas a larger concentration accelerates Ag diffusion into the grain boundaries making them non-superconducting. As mentioned earlier very high values of $J_c = 18500\,A.cm^{-2}$ (Salma *et al* 1989) and J_c of $17000\,A.cm^{-2}$ (Jin *et al* 1988a,b) have been obtained in bulk Y_{123} by the so-called liquid phase and melt-texturing process respectively which yield highly oriented grain structure. In both processes, however, the compact is heated to high temperature 1100–1300°C. The adoption of these techniques for wire fabrication will put new demand on the suitability of the sheath material.

4. Conclusions

For most of the rare earth-substituted Ag-clad wires of $R_1Ba_2Cu_3O_{7-x}$ compounds, J_c has been found to be limited to $66\,A.cm^{-2}$ (77 K) using the powder-in-tube method. An improved packing density and a thicker Ag sheath have been found beneficial for improving J_c probably because of a better density obtained in the sintered core and a reduced loss of oxygen during sintering and hence a better O_2-stoichiometry. Much better density and a highly oriented grain structure is, however, essential to obtain high J_c in these metal clad wires or tapes.

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References

Deutscher G, Entin-Wohlman O, Fishman S and Shapira Y 1980 *Phys. Rev.* **B21** 5041

Dinger T R, Worthington T K, Gallagher W J and Sandstrom R L 1987 *Phys. Rev. Lett.* **58** 2687

Flukiger R, Muller T, Goldaker W, Wolf T, Seibt T, Apfelstedt I, Kupfer H and Schauer W 1988 *Physica* **C153–155** 1574

Glowacki B A and Evetts J E 1987 *MRS Meeting, Boston, Paper AA* 4.58

Hagen S, Jing T W, Wang Z Z, Horwath J and Ong N P 1988 *Phys. Rev.* **B37** 7928

Imanaka N, Saito F, Imai H and Adachi G 1989 *Jpn. J. Appl. Phys.* L580

Jin S, Tiefel T H, Sherwood R C, van Dover R B, Davis M E, Kammlott G W and Fastnacht R A 1988a *Phys. Rev.* **B37** 7850

Jin S, Tiefel T H, Sherwood R C, Davis M E, van Dover R B, Kammlott G W, Fastnacht R A and Keith H D 1988b *Appl. Phys. Lett.* **52** 2074

Johnson Jr D W and Grader G S 1988 *J. Am. Ceram. Soc.* **71** C-291
Kawashima M, Nagata M, Hosoda Y, Takano S, Shibuta N, Mukai H and Hikata T 1989 *IEEE Trans. Magn.* **25** 2168
Kohno O, Ikeno Y, Sadakata N and Goto K 1988 *Jpn. J. Appl. Phys.* **27** L77
Martin S, Fiony T, Fleming R M, Schncemeyer L F and Waszczak J V 1988 *Phys. Rev. Lett.* **60** 2194
Matsumoto T *et al* 1989 *ISTEC Workshop on superconductivity, Japan*, p. 111
Okada M, Okayama A, Morimoto T, Matsumoto T, Aihara K and Matsuda S 1988 *Jpn. J. Appl. Phys.* **27** L185
Salama K, Solvamanickam V, Gao L and Sun K 1989 *Appl. Phys. Lett.* **54** 2352
Sharma R G, Reddy Y S, Jha S R, Kundra K D and Suri D K 1988a *Pramana–J. Phys.* **30** L75
Sharma R G, Reddy Y S, Jha S R and Dubey S S 1988b *Pramana–J. Phys.* **30** L81
Sharma R G, Reddy, Y S and Jha S R 1988c *Rev. Solid State Sci.* **2** 509
Taylor K N R, Shepherd M, Matthews D N, Russel G J, Bailey A D and Sealy K 1988 in *High temperature superconductors II*, (eds) D W Capone II, W H Butler, B Batlogg and C W Chu (MRS Publication) p. 247
Wang Z Z and Ong N P 1988 *Phys. Rev.* **B38** 7160