The synthesis of evaporated thallium-based superconducting thin films using an improved thalliation process

H. C. LAI
Material Research Laboratories, Industrial Technology Research Institute, Hsinchu, 31015, Taiwan

C. R. M. GROVENOR
Department of Materials, Oxford University, Parks Road, Oxford OXI 3PH, UK

Superconducting Tl–Ca–Ba–Cu–O (TCBCO) thin films, about 1 μm thick, have been prepared on (1 0 0) MgO substrates using a thermal evaporation and improved two-step annealing process involving final thalliation under controlled Tl_2O vapour pressure in a quartz reaction tube. The Tl_2O vapour pressure was changed by adjusting the position of a Tl_2O_3-containing boat, thus altering the boat temperature from 740–780 °C when the furnace temperatures were between 830 and 850 °C. The superconducting properties of TCBCO films are strongly dependent on the Tl_2O vapour pressure and oxygen partial pressure. Thalliated $Tl_2Ca_1Ba_2Cu_2O_x$ and $Tl_2Ca_2Ba_2Cu_3O_x$ films with T_{c0}'s of up to 110 and 117 *K*, respectively, and $J_{c,77\,K}$'s measured over large areas of up to 1×10^4 A cm^{-2}, have been obtained. A low-temperature annealing process after thalliation does not seem to offer significant advantages for these films, which is thought to be due to the loss of thallium. It is also found that measuring J_c values on narrow microbridge structures can give a false impression of the overall quality of polycrystalline thin-film samples.

1. Introduction

After the discovery of the Tl–Ca–Ba–Cu–O (TCBCO) superconductors [1] the possibility for widespread commercial exploitation immediately become an important area of worldwide research. Large-area and high-quality TCBCO thin films are of considerable technological importance in microwave applications. High-quality superconducting TCBCO films can now be grown with good reproducibility by a variety of methods [2–5]. However, the high toxicity of the thallium compounds and problems with control of Tl_2O vapour pressure has limited the practical commercial applications of TCBCO thin films. From the paper by Cubicciotti and Keneshea [6], Tl_2O_3 vaporizes according to the equilibrium, $Tl_2O_{3(s)} = Tl_2O_{(g)} + O_{2(g)}$. Hence the decomposition of $Tl_2O_{3(g)}$ to $Tl_2O_{(g)}$ and $O_{2(g)}$ can be retarded by increasing the oxygen partial pressure. In 1990, Aselage *et al.* [7], after a series of isothermal equilibrium experiments in a pseudoternary system, indicated that the superconducting TCBCO phases are unstable in an isothermal equilibrium fabrication process and suggested that the stable superconducting TCBCO phases can exist only in Tl_2O partial pressures "lower" than the isothermal vapour pressure of Tl_2O over condensed Tl_2O_3. There are many papers on the necessity and importance of controlling the thalliation ambient, but with conflicting results [8, 9]. Recently, a paper by Ahn *et al.* [10] has studied the effect of oxygen partial pressure on phase formation in the TCBCO system and suggested a reasonable phase diagram. It seems that the best J_c values may be dependent on processing in a narrow temperature range and thalliation ambient. We have investigated thalliation of thallium-free precursor films with the Tl_2O vapour pressure under precise control following the work of Deluca *et al.* [11]. A low-temperature anneal in oxygen after thalliation is supposed to be helpful in improving the superconducting properties of TCBCO films [12, 13] and this has also been studied with little sign of improvement in the properties of our films.

2. Experimental procedure

Precursor CaBaCu oxide films with metallic ratio of Ca:Ba:Cu = 2:2:3, about 1 μm thick, were prepared on (1 0 0) MgO by a simple evaporation technique as described elsewhere [14], and inserted in a quartz reaction tube, as schematically shown in Fig. 1. The Tl_2O vapour pressure was changed by adjusting the position of a Tl_2O_3-containing boat (Tl-boat) thus altering the boat temperature from 740–780 °C at film temperatures of from 830–850 °C. Films were annealed for 10–40 min in air or oxygen ambient (oxygen flow rate about 35 cm^3 min^{-1}) with a final air quench. The tube was loaded by placing the Tl-boat at the

0022–2461 © *1995 Chapman & Hall*

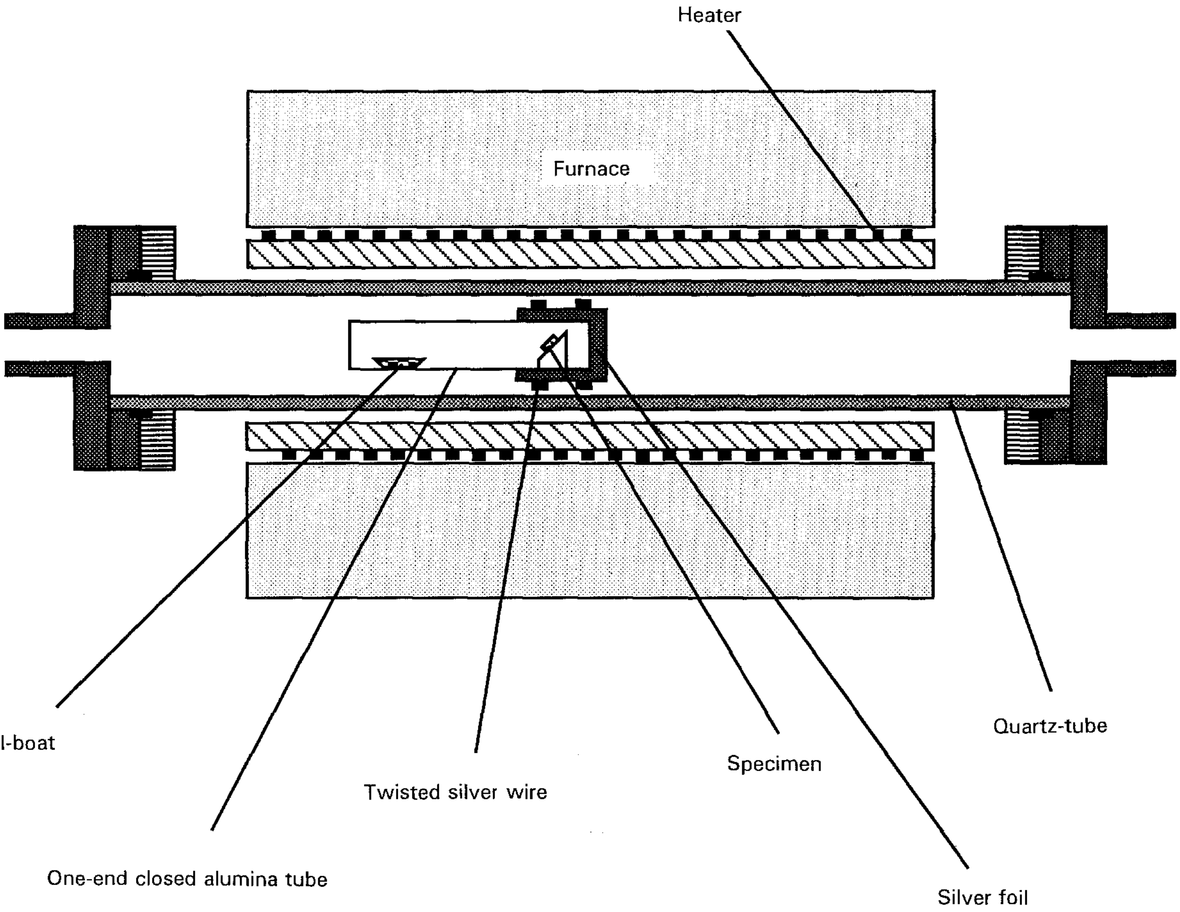


Figure 1 Schematic picture of the experimental design.

closed end and the sample tray near the open end. This furnace design follows the work of Deluca *et al.* [11] on the importance of controlled Tl_2O vapour pressures during thalliation. Low-temperature annealing was carried out in the presence of bulk $Tl_2Ca_1Ba_2Cu_2O_x$ samples creating an equilibrium Tl_2O vapour pressure over the films in silver-covered Al_2O_3 crucibles.

Resistance/temperature (R/T) plots were obtained using the conventional four-point contact technique with a measuring current of 100 μA. Critical current densities, J_c, were measured using a criterion of $1\ \mu V\,cm^{-1}$ over $1 \times 0.5\ cm^2$ area. Some films were patterned to meander-type structures using standard photolithography techniques and wet chemical etching for comparison. Grain morphologies and phase purities were analysed by X-ray diffraction (XRD) and scanning electron microscopy (SEM) equipped with energy dispersive X-ray analysis (EDS).

In our previous work we established that thalliation at 830 °C for 40 min is a favourable condition for obtaining reasonably uniform and relatively phase-pure $Tl_2Ca_2Ba_2Cu_3O_x$ films. Hence this condition has been selected as a standard for finding the effects of altering thallium vapour pressure and thalliation ambient. The typical Tl-boat temperatures chosen for comparing the effect of different thallium vapour pressures are between 740 and 780 °C. This range is limited by the size of the Tl-boat and the temperature profile of the furnace.

3. Results and discussion

3.1. The effect of thalliation ambient

For looking into the effect of oxygen concentration on the thalliation ambient, films prepared at 830 °C for 40 min in air and oxygen with a Tl-boat temperature of 780 °C were chosen for comparison. From XRD data, 2122 is the primary phase and there is no significant differences for films thalliated in air or in oxygen. This is consistent with the diagram predicted by Ahn *et al.* [10]. However, as shown in Fig. 2, the microstructure of a thin film thalliated in air consists primarily of loosely packed regions with isolated voids. Films thalliated in oxygen have better surface wetting characteristics, and are composed mostly of closely packed small grains with less pronounced boundaries. The values of T_{c0} are 109 K in oxygen and 106 K in air. The values of normal state resistance in oxygen and in air are 2 and 9 Ω, respectively, at 140 K, indicating that normal state resistance of the film thalliated in air is much greater than that of the film prepared in oxygen. In addition, a large area ($1 \times 0.5\ cm^2$) J_c value in excess of $2 \times 10^4\ A\,cm^{-2}$ at 20 K and about $1 \times 10^4\ A\,cm^{-2}$ at 77 K is measured in the film prepared in oxygen, which is much better than that measured in the film prepared in air. In all of the thalliation processes used in this work, the Tl_2O vapour pressure above the films is much lower than the equilibrium vapour pressure above Tl_2O_3 at the film temperature, because the thallium vapour is created by vaporization above the colder Tl-boat and the

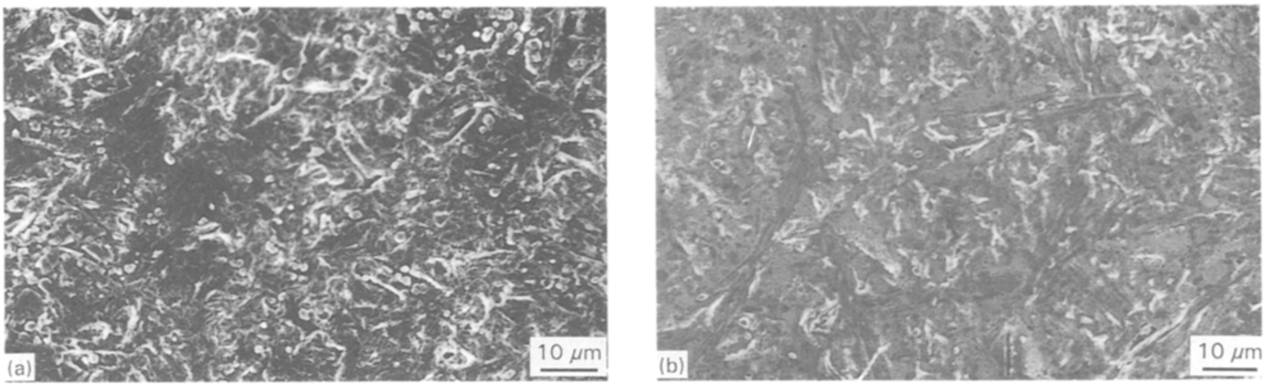


Figure 2 Scanning electron micrographs of TCBCO films thalliated at 830 °C for 40 min with a Tl-boat temperature of 780 °C, (a) in air and (b) in oxygen.

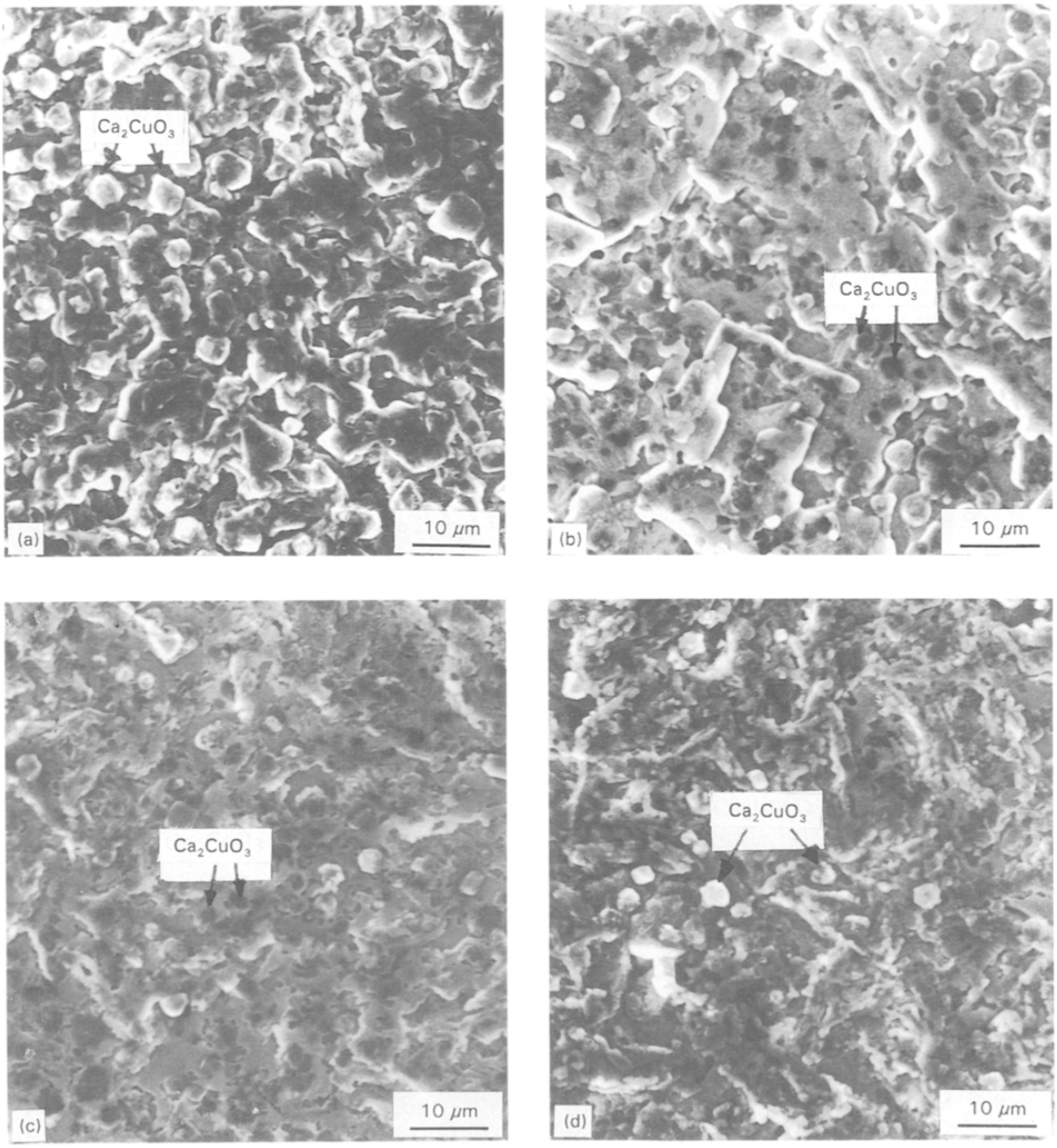


Figure 3 Scanning electron micrographs of TCBCO superconducting films thalliated in air at 830 °C for 40 min with different Tl-boat temperatures: (a) 740 °C, (b) 760 °C, (c) 770 °C, and (d) 780 °C. 760 and 770 °C seem to be the temperatures at which the optimum Tl_2O vapour pressure is produced.

diffusion of this vapour into the hotter part of the furnace. The use of an oxygen ambient must further reduce the Tl_2O partial pressure. It seems, therefore, that the optimum thalliation conditions for these films is not with a large excess of thallium in the vapour phase, in agreement with the work of Aselage *et al.* [7].

3.2. The effect of Tl_2O vapour pressure

Thalliation at 830 °C for 40 min in 1 atm oxygen pressure has been chosen for comparison.

Fig. 3 shows a series of scanning electron micrographs of superconducting films formed at different Tl-boat temperatures. At lower temperatures (740 °C), as shown in Fig. 3a, we can see loosely packed and irregular TCBCO crystallites decorated with a large number of rough $CaCu_2O_3$ particles about 5 μm across, embedded in voids or at grain boundaries. At temperatures of 760 and 770 °C, which seems to be the temperature at which the optimum Tl_2O vapour pressure is produced to aid the growth of thin films, a melted and smoothly terraced morphology decorated by spheroidal Ca_2CuO_3 or $CaCu_2O_3$ particles is obtained as shown in Fig. 3b and c. At higher temperature (780 °C) the grains grow as large irregular interconnected platelets, and small Ca_2CuO_3 grains with spheroidal morphology decorate the surface. At temperatures of 740 and 760 °C, the Tl_2O vapour pressure is favourable for forming the 2223 phase; however, in our experience it is not possible to form the 2223 phase at Tl-boat temperatures lower than 740 °C as a result of the lack of thallium. At temperatures of 770 and 780 °C, 2122 or 1223 is the primary phase. The 1223 phase always co-exists with the two thallium layer phases and can be the dominant superconducting phase, e.g. at 770 °C.

Fig. 4 shows the R/T plot for these four films, revealing that reasonably good quality 2223 films with T_{c0}'s of greater than 112 K and $J_{c,77\,K}$'s, measured over large areas, of about 2×10^3 A cm^{-2} can be prepared at a Tl-boat temperature of 760 °C. 2122 films with T_{c0}'s of 110 K and $J_{c,77\,K}$'s in excess of 9×10^3 A cm^{-2} can be obtained at a Tl-boat temperature of 770 °C. Those films prepared at a Tl-boat temperature of 740 °C show a drop in resistance; however, the R/T curve always has a long tail and rarely reaches zero resistance. The similar T_c's for both 2122 and 2223 films are thought to be due to the very small amounts of 2122 at the 2223 grain boundaries, as observed in similar films by Grovenor *et al.* [15].

It seems that the thalliation condition in which 2122 is the only superconducting phase as predicted by Ahn *et al.* [10] can also produce reasonably good quality 2223 films by careful control of the Tl_2O vapour pressure. Hence, a shifted boundary between the 2122 and 2223 phase regions expected by Ahn *et al.* will happen when the effect of Tl_2O vapour pressure is taken into account.

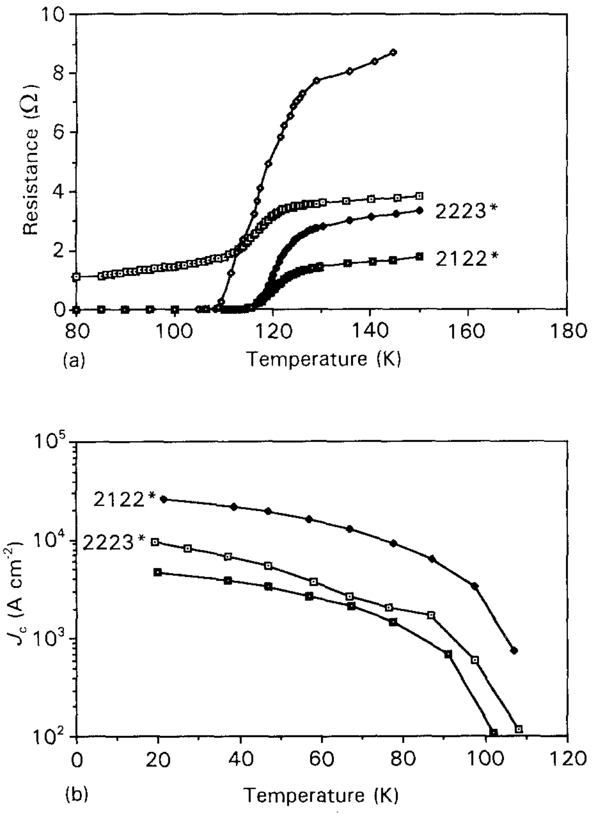


Figure 4 Resistance/temperature plots for films thalliated in air at 830 °C for 40 min with different Tl-boat temperatures, revealing that reasonably good-quality films with 2122 or 2223 as primary phase can be obtained by adjusting Tl_2O vapour pressure. (a) (☐) 740 °C, (◆) 760 °C, (■) 770 °C, (◇) 780 °C. (b) (☐) 760 °C, (◆) 770 °C, (■) 780 °C. (★) Primary phase.

3.3. The effect of thalliation duration

As described by Lai *et al.* [14], thalliation time has some influence on the surface morphology and superconducting phase formation. It is worthwhile repeating this experiment with Tl_2O vapour pressure under precise control. Three thalliation times of 30, 40 and 45 min have been used with a thalliation temperature of 830 °C and a Tl-boat temperature of 770 °C in air for comparison of composition and superconducting properties.

Fig. 5 shows the XRD data for these films, revealing that at a shorter thalliation time (30 min), only poorly textured films are formed containing 2122, 1223 and 2223 mixed phases. After a further 10 min treatment, a reasonably high-purity 2122 film has been produced, although trace of impurities of Ca_2CuO_3 or $CaCu_2O_3$ are present. The 2223 phase, which is supposed to be produced by reaction of 2122 with excess calcium and copper [16], is formed after longer thalliation, but at the price of poorly connected granulated microstructure (not shown here). This is the reason why a relatively higher temperature and shorter thalliation time needs to be used for preparing reasonably good-quality 2223 films, as described in Section 3.4. The corresponding R/T and J_c/T plots, as shown in Fig. 6, reveal that T_{c0}'s of 104 K (30 min), 110 K (40 min), and 92 K (45 min), and $J_{c,77\,K}$'s measured over large areas, of about 1.2×10^3 A cm^{-2} (30 min) and about 1×10^4 A cm^{-2} (40 min) have been obtained. 2122 thin films containing a small component of the 1223 superconducting phase prepared after 40 min annealing have surprisingly high J_c values.

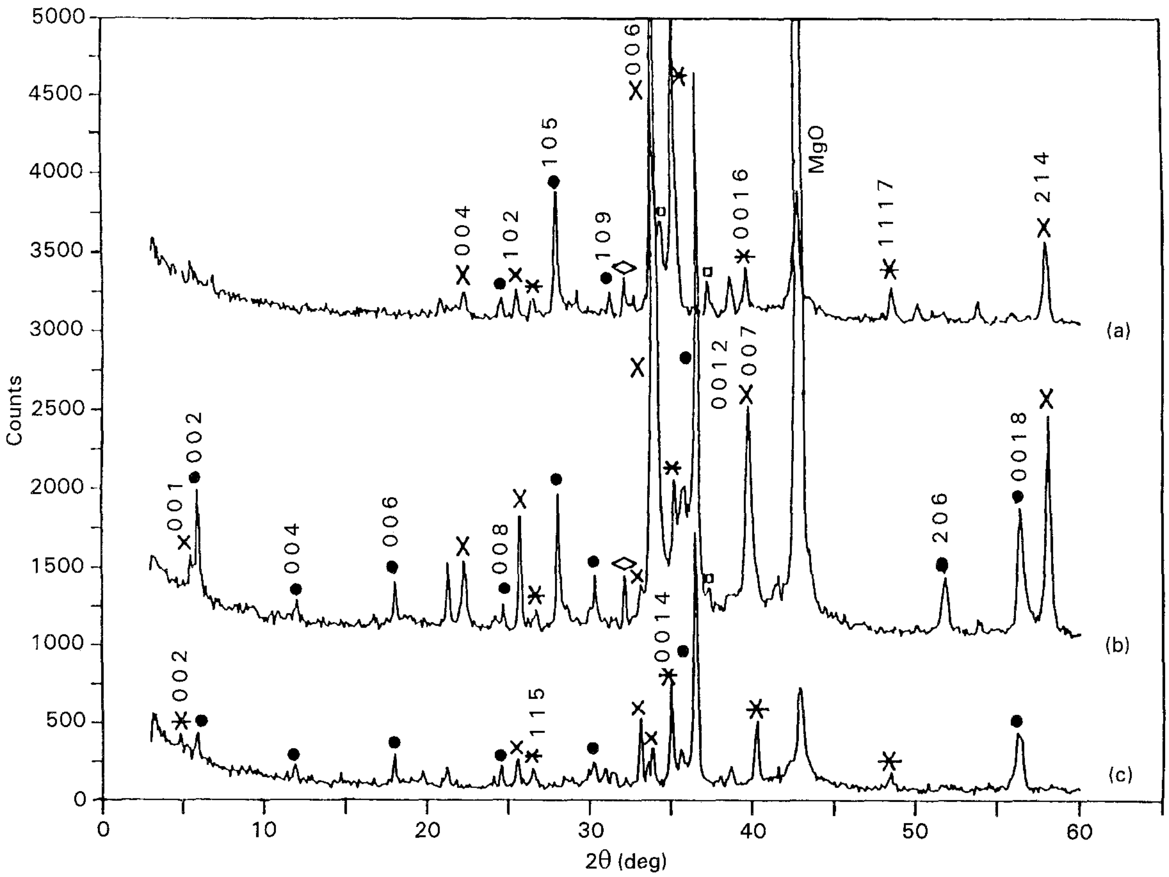


Figure 5 XRD data for TCBCO films thalliated in air at 830 °C for different durations: (a) 30 min, (b) 40 min and (c) 45 min with a Tl-boat temperature of 770 °C. After 30 min, 2223 is the primary phase. After a further 10 min, 2122 is the primary phase. A mixture of 2122 and 2223 phases is formed after a further 5 min annealing. The 1223 phase always exists with these two thallium-layer phases. (●) 2122, (★) 2223, (×) 1223, (□) $CaCu_2O_3$, (◇) Ca_2CuO_3.

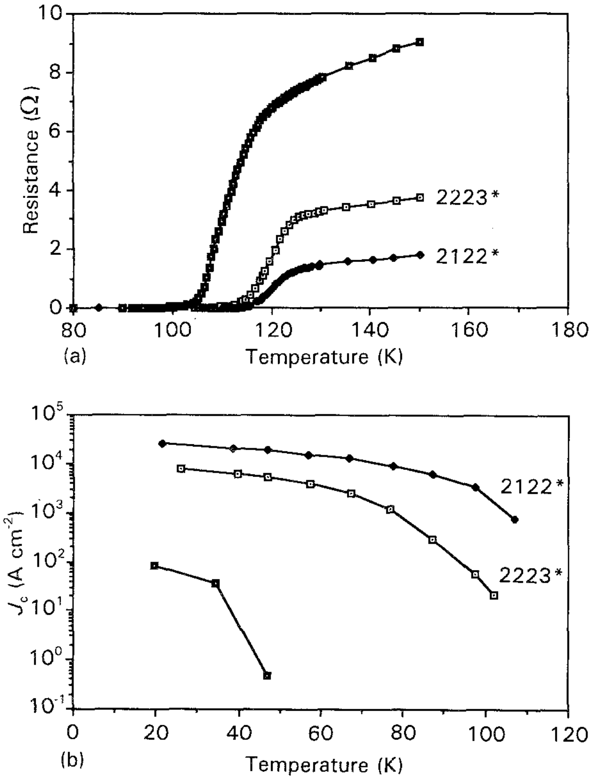


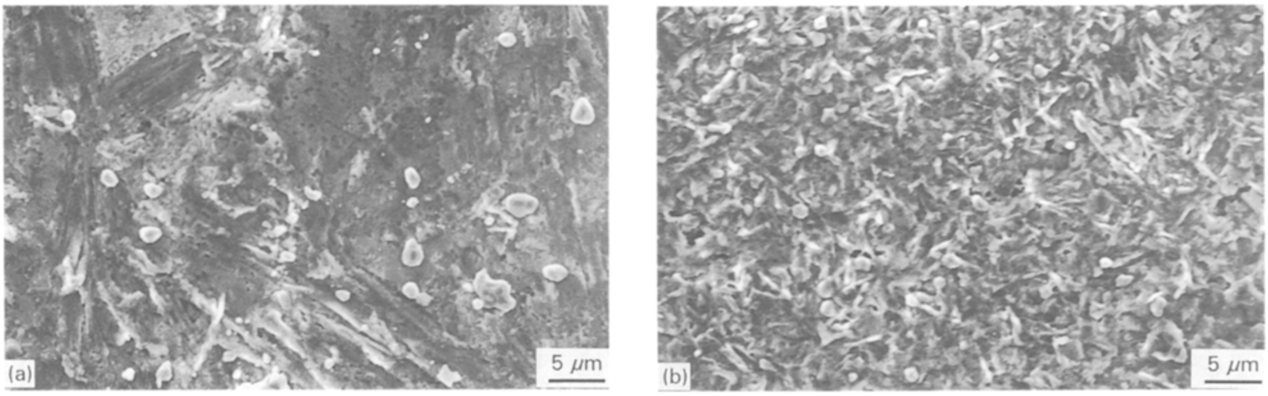
Figure 6 (a) Resistance/temperature, and (b) critical current density/temperature plots for films with different thalliation durations, revealing that reasonably good-quality films with 2122 or 2223 as primary phase can be obtained by changing the thalliation time. Temperature, 830 °C, time: (□) 30 min, (◆) 40 min, (■) 45 min. (★) Primary phase.

1223 phases always exist after these thalliation processes. Recently, Deluca *et al.* [17] have shown that the cation stoichiometry $Tl_xCa_2Ba_2Cu_3$ in the presence of silver can produce the "1223" phase, as the values of x are between 0.65 and 1.00. It seems that the conditions for forming 1223 are much less sensitive to Tl_2O vapour pressure and thalliation temperature than the 2122 and 2223 phases. This is supposed by the fact that we observe 1223 phase always coexisting with 2122 or 2223 phases in films prepared under widely different thalliation conditions.

3.4. Higher thalliation temperatures in oxygen for high-quality 2223 thin films

A series of experiments on higher thalliation temperatures and different durations in oxygen have been investigated for obtaining uniform and high-quality 2223 films. The Tl-boat temperature was kept at about 775 °C.

Fig. 7 shows the SEM morphologies of thin films thalliated at 830, 840 and 850 °C for 40, 20 and 10 min, revealing different microstructures from irregular cheese-like melted structure to melted-sheet type crystal-growth morphology. It is found that those films prepared at 830 °C for 40 min and 850 °C for 10 min have better surface wetting characteristics and are composed mostly of closely packed small grains with less pronounced boundaries. However, the sample thalliated at 840 °C for 20 min has shown partially



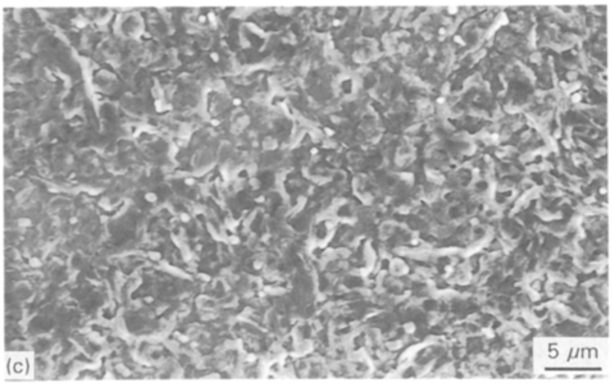


Figure 7 Scanning electron micrograph of TCBCO film thalliated in oxygen with Tl-boat temperature of 775 °C at (a) 830 °C for 40 min, (b) 840 °C for 20 min, and (c) 850 °C for 10 min, revealing different microstructures from irregular cheese-like melted structure to melted-sheet type crystal-growth morphology.

needle-like structure with voids through to the substrate.

The XRD patterns from these films are shown in Fig. 8. In the case of the film thalliated at 830 °C for 40 min, as shown in Fig. 8a, 2122 is the majority phase, only a few traces of 2223 were observed. Fig. 8b and c show that all the peaks could be assigned to 2223 phase. These films seem uniform in composition (from broad-area and spot EDS analysis). The observation of no low-angle (~ 5 °) XRD peak is thought to be due to the very fine grain size. The corresponding R/T and J_c/T curves are shown in Fig. 9, revealing that the T_{c0}'s of these films are 110, 88 and 117 K, respectively, and a value of large-area (1×0.5 cm^2)

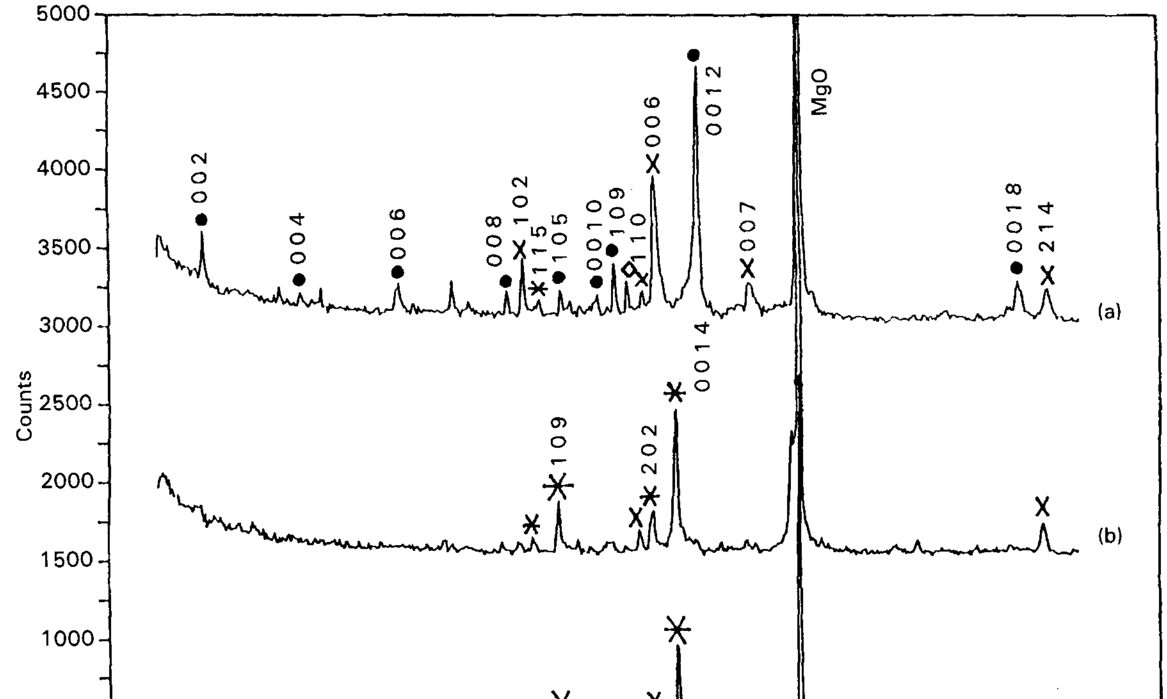


Figure 8 XRD data from a TCBCO film thalliated in oxygen with a Tl-boat temperature of 775 °C at (a) 830 °C for 40 min, (b) 840 °C for 20 min and (c) 850 °C for 10 min, revealing that 2223 is the primary phase when the films thalliated at higher temperature (840 and 850 °C) for shorter heat-treatment times (20 and 10 min). (●) 2122, (★) 2223, (×) 1223, (◇) Ca_2CuO_3.

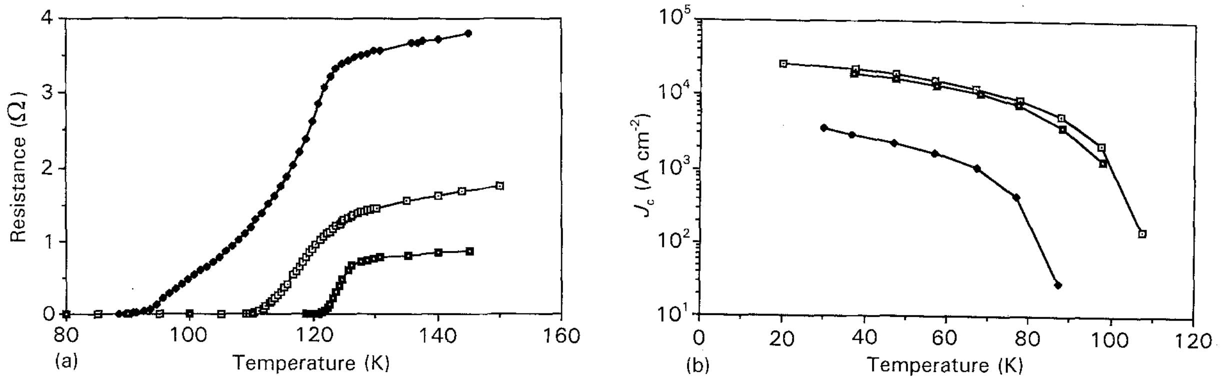


Figure 9 (a) Resistance/temperature, and (b) critical current density/temperature plots of films with different thalliation conditions, revealing that the condition with higher temperature (850 °C) and shorter time (10 min) is favourable for making reasonably good-quality 2223 films in oxygen. (□) 830 °C/40 min (780 °C), (◆) 840 °C/20 min (775 °C), ■) 850 °C/10 min (775 °C).

transport J_c of up to 1×10^4 A cm^{-2} at 77 K for the pure 2223 film (thalliation at 850 °C for 10 min) can be obtained.

3.5. The effect of low-temperature annealing in oxygen

Films thalliated at 830 °C for 40 min in air or oxygen with a Tl-boat temperature of 780 °C have been soaked in oxygen at 400 and 750 °C for 6 h and 30 min respectively. For the case of a soak at 400 °C for 6 h, from the XRD analysis shown in Fig. 10, the overall phase composition of the films seems fairly stable, and is not much affected by the low-temperature annealing. However, the corresponding R/T and J_c/T plots, as shown in Fig. 11, indicate that the superconducting properties of the thin films are degraded by the soak. Similar results have been found in the

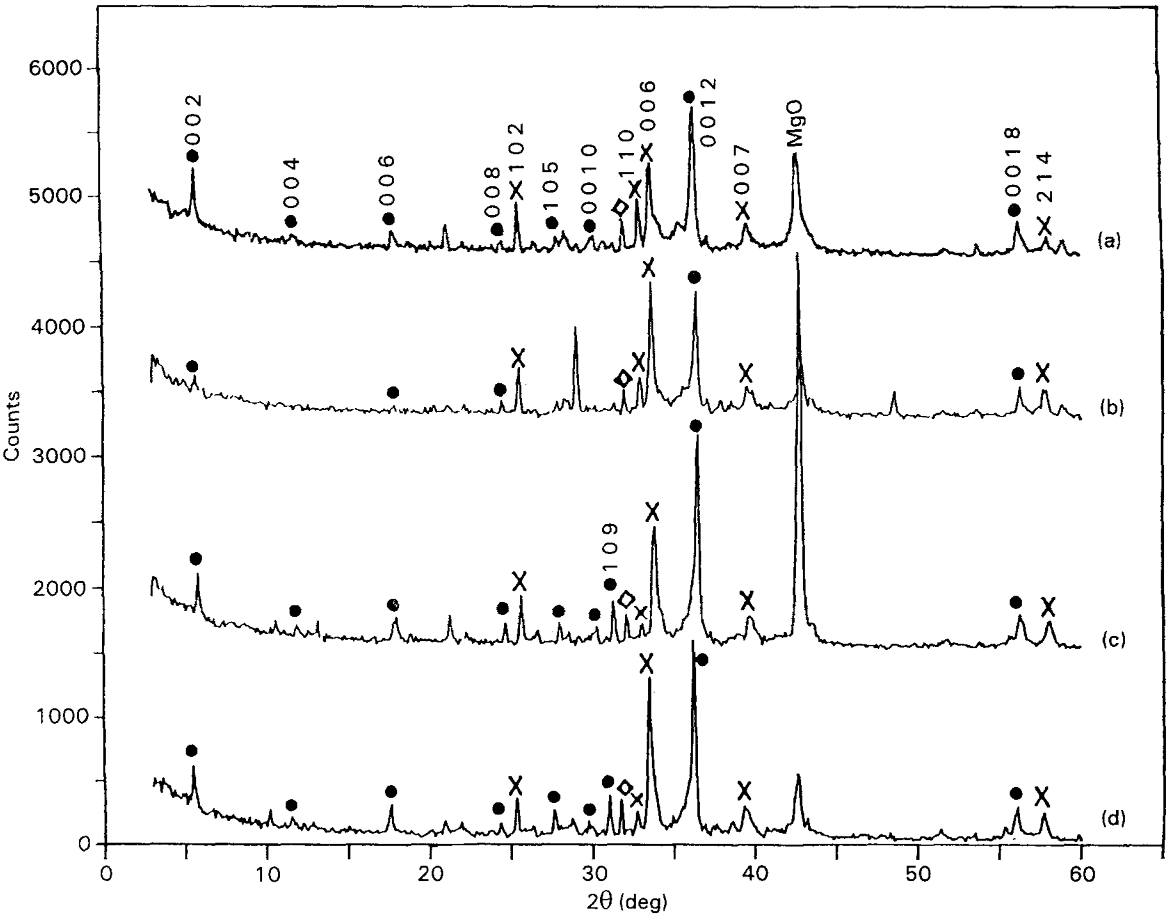


Figure 10 XRD data from TCBCO films thalliated at 830 °C for 40 min with a Tl-boat temperature of 780 °C in different ambients with or without low-temperature annealing at 400 °C for 6 h in oxygen: (a) thalliation in "air" before low-temperature annealing, (b) thalliation in "air" after low-temperature annealing, (c) thalliation in "oxygen" before low-temperature annealing and (d) thalliation in "oxygen" after low-temperature annealing, revealing that there are obvious differences in films before and after low-temperature annealing. (●) 2122, (×) 1223, (◇) Ca_2CuO_3.

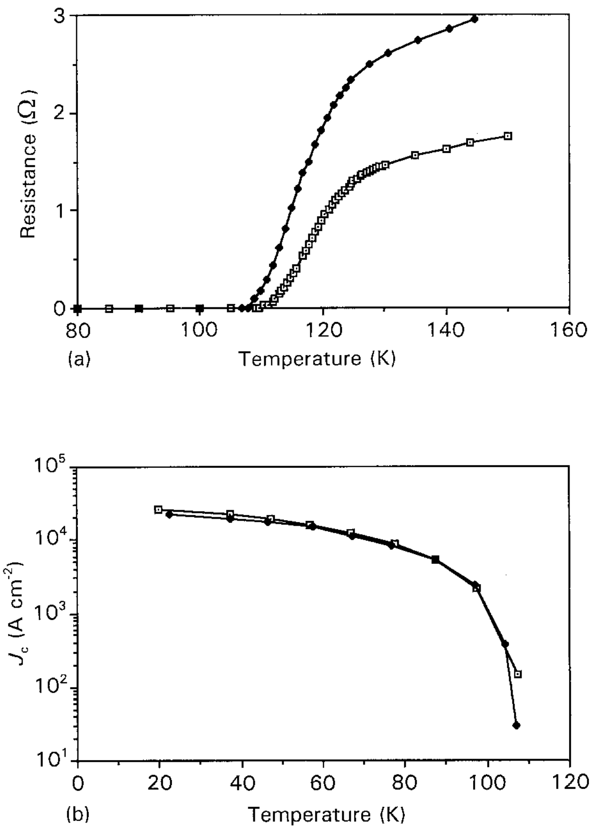


Figure 11 (a) Resistance/temperature, and (b) critical current density/temperature plots for a film thalliated in air (□) before and after (◆) after low-temperature annealing at 400 °C for 6 h in oxygen.

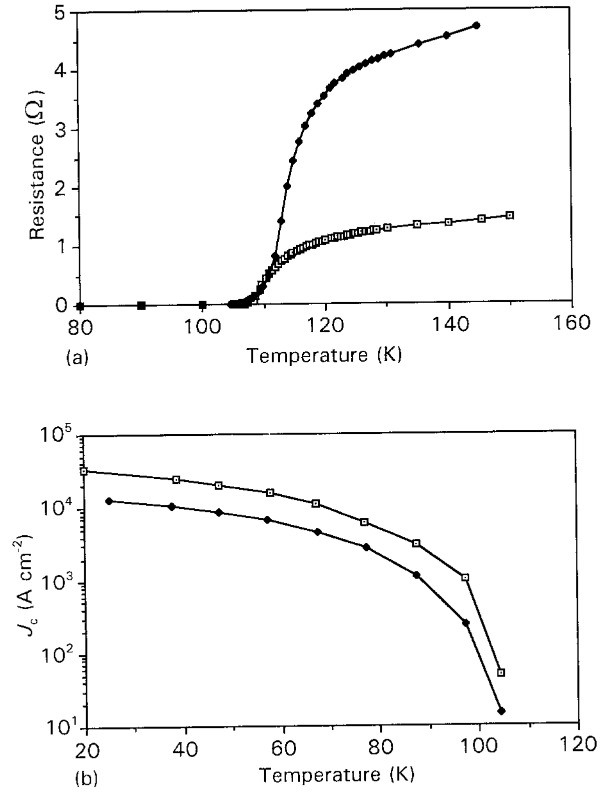


Figure 12 (a) Resistance/temperature, and (b) critical current density/temperature plots for a film thalliated in air (□) before and (◆) after low-temperature annealing at 750 °C for 30 min in oxygen.

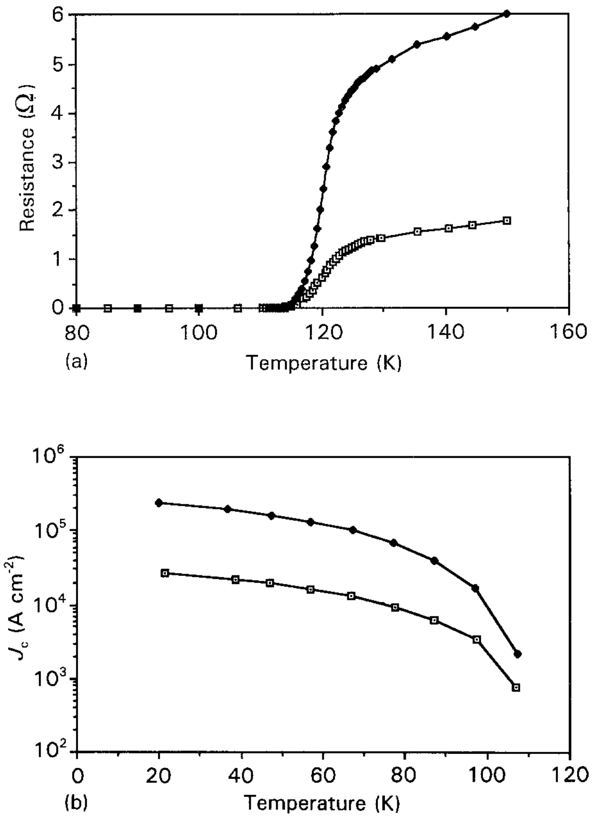


Figure 13 (a) Resistivity/temperature, and (b) critical current density/temperature plots for a TCBCO film (□) before and (◆) after patterning.

case of a soak at 750 °C for 30 min. A comparison of resistive and transport properties of a film before and after soaking, as shown in Fig. 12, reveals that there is a degradation in the superconducting properties. The degradation of superconducting properties is thought to be due to the loss of thalliation.

3.6. Does patterning the films affect the superconducting properties?

Fig. 13 shows typical R/T and J_c/T curves from a film, thalliated at 830 °C for 40 min in oxygen with a Tl-boat temperature of 760 °C, in unpatterned and patterned state. Although these samples were washed in acetone and running water during patterning, little modification of the value of T_{c0} has been found. This shows that these TCBCO films do possess good stability in various environments. The transport J_c measured on one of these films reveals an interesting result with $J_{c,77\,K}$'s of greater than 6×10^4 A cm^{-2} for a 60 μm wide track, much higher than the value measured on the whole of the unpatterned films. It is found that measuring only narrow microbridge structures can give a false impression of the overall quality of a polycrystalline thin-film sample. We assume that this is because it is possible for the bridge to lie in a particularly good region of inhomogeneous films.

4. Conclusion

An easily operated thalliation process adjusting the position of a Tl_2O_3-containing boat has been used to control Tl_2O vapour pressure. The superconducting properties of TCBCO films are strongly dependent on the Tl_2O vapour pressure and oxygen partial pressure. $Tl_2Ca_2Ba_2Cu_3O_x$ films with T_{c0}'s of up to 117 K and $J_{c,77K}$'s (1×0.5 cm^2) of up to 1×10^4 A cm^{-2} have been obtained. The effect of low-temperature annealing is still not well understood and seems to degrade the film properties in this work. It is also shown that measuring J_c values on narrow microbridge structures can give a false impression of the overall quality of polycrystalline thin-film samples.

Acknowledgements

H. C. Lai is a receipt of an Overseas Research Scholarship. The authors thank Dr P. J. Dobson for his constant advice on the patterning equipment and experimental processes. Professor Sir Peter Hirsch, FRS, is gratefully acknowledged for the provision of laboratory facilities. This work was supported in part by the SERC under Grant GR/F 53139, and the Ministry of Economic Affairs, Taiwan, under Contract 38R2100 to the Industrial Technology Research Institute.

References

1. Z. Z. SHANG and A. M. HERMANN, *Nature* **332** (1988) 138.
2. Z-Y. SHEN, P. PANG, C. WILKER, D. B. LAUBACHER, W. L. HOLSTEIN and C. F. CARTER III, *IEEE Trans. Appl. Supercond.* **3** (1993) 2832.
3. A. LAUDER, C. WILKER, D. J. KOUNTZ, W. L. HOLSTEIN and D. W. FACE, *ibid.* **3** (1993) 1683.
4. D. J. KOUNTZ, P. L. GAI, C. WILKER, W. L. HOLSTEIN and F. M. PELLICONE, *ibid.* **3** (1993) 1222.
5. W. L. HOLSTEIN, L. A. PARISI, C. WILKER and R. B. FLIPPEN, *ibid.* **3** (1993) 1197.
6. D. CUBICCIOTTI and F. J. KENESHEA, *J. Phys. Chem.* **71** (1967) 808.
7. T. L. ASELAGE, J. A. VOIGT and K. D. KEEFER, *J. Am. Ceram. Soc.* **73** (1990) 3345.
8. Y. SAITO, T. NABATAME and J. CHEUNG, *Jpn J. Appl. Phys.* **30** (1991) L820.
9. H. ADACHI, K. WASA, Y. ICHIKAWA, K. HIROCHI and K. SETSUNE, *J. Crystal Growth* **91** (1988) 352.
10. B. T. AHN, W. Y. LEE and R. BEYERS, *Appl. Phys Lett.* **60** (1992) 2150.
11. J. A. DELUCA, M. F. GARBAUSKAS, R. B. BOLON, J. G. McMULLEN, W. E. BALZ and P. L.KARAS, *J. Mater. Res.* **6** (1991) 1415.
12. G. S. GINLEY, J. F. KWAK, R. P. HELLMER, R. J. BAUGHMAN, E. L. VENTURINI, M. A. MITCHELL and B. MOROSIN, *Phys. C* **156** (1988) 592.
13. K. ZHANG, E. P. BOYD, B. S. KWAK, A. C. WRIGHT and A. ERBIL, *Appl. Phys. Lett.* **55** (1989) 1258.
14. H. C. LAI, K. D. VERNON-PARRY, J. D. CHERN and C. R. M. GROVENOR, *Supercond. Sci. Technol.* **4** (1991) 306.
15. C. R. M. GROVENOR, L. T. ROMANO, K. P. MINGARD, H. C. LAI and K. D. VERNON-PARRY, *J, Mater. Res.* **6** (1991) 1408.
16. E. RUCKENSTEIN and C. T. CHEUNG, *ibid.* **4** (1989) 1116.
17. JOHN A. DELUCA, PAMELA L. KARAS, J. E. TKACZYK, PETER J. BEDNARCZYK, MARY F. GARBAUSKAS, CLYDE L. BRIANT and DONALD B. SORENSEN, *Phys. C* **205** (1991) 21.

Received 21 December 1993
and accepted 9 June 1994