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Electrochemical synthesis of Tl-based high T_c single-phase superconductor thin films

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Abstract. Co-deposition of the Tl-based superconductors using electrodeposition technique was successfully carried out. Different processing parameters such as deposition potential, current density, deposition period etc were studied. The Tl-based alloyed thin films were deposited at a constant potential of – 1·25 V with respect to SCE electrode onto silver substrates and oxidized at 850°C in oxygen atmosphere. The samples thus prepared showed superconducting behaviour below 122·5 K and the critical current density was $1{\cdot}5 \times 10^3$ A/cm^2. Electrochemical synthesis of Tl-based high T_c single-phase superconductor thin films is also reported.

Keywords. Superconductivity; Tl–Ba–Ca–Cu thin films; X-ray diffraction; resistivity.

1. Introduction

Since the discovery of high temperature superconductivity above 100 K in the Tl–Ba–Ca–Cu–O system (Sheng and Hermann 1988), attempts have been made to grow single crystals of Tl–Ba–Ca–Cu–O with higher values of T_c. The system exists with a variety of phases with both single and double layer Tl–O structures and multiple Cu–O layers from 1 to 5 (Raveau *et al* 1991; Toradi 1992). Of the various phases, the (2223) phase with three Cu–O layers has the highest superconducting transition temperature.

The Tl-based superconductors are considered to be the most likely candidate for use in underground power transmission lines, which needs film thickness of the order of 1 to 10 μm and above. Tl-based films with such thickness can be fabricated by a range of processes: powder-in-tube method (Okada *et al* 1991), aerosol deposition (Shing *et al* 1995), electrodeposition (Bhattacharya *et al* 1993), sol-gel method (Jian *et al* 1993) and screen printing and painting. Electrodeposition is a simple, low-cost and efficient method capable of producing high temperature superconducting films of any shape and size. Electrodeposition is a room temperature technique, totally preventing any inhalation of toxic thallium oxide vapours. The method has been used to produce YBCO, BSCCO, and TBCCO thin films by various research groups (Pawar and Mujawar 1991; Bhattacharya *et al* 1992; Pawar *et al* 1993a, b, 1994; Bhattacharya and Blaugher 1994).

The present paper reports the electrodeposition of Tl-based high T_c single-phase thin films from a nonaqueous bath onto silver substrates. The different processing parameters such as deposition potential, current density and deposition period have been studied and reported. The electrodeposited alloyed thin films are then oxidized at high temperature and tested for their superconducting properties and X-ray diffraction measurements.

2. Experimental

The chemical constituents of electrodeposition bath were adjusted empirically to produce stoichiometric alloyed films. The deposition bath was prepared using reagent grade nitrates of thallium, barium, calcium and copper dissolved in dimethyl sulphoxide. The concentrations were 33, 60, 40 and 66 mM respectively. Electrodeposition set-up consisted of a conventional three-electrode system with saturated calomel electrode (SCE) as a reference electrode, Ag foil as working electrode and graphite plate as the counter electrode. The Tl-based alloy was electrodeposited onto mirror-polished silver substrate using a scanning potentiostat/galvanostat (EG & G model 362) under potentiostatic conditions. An Omnigraphic X–Y recorder (model 2000) was used for recording the voltammogram and hence the electrodeposition potential. Electrodeposition was carried out at an ambient temperature.

The electrodeposited alloyed films were annealed at 850°C for 50 min under flowing oxygen. The furnace was then turned off and slowly cooled down to room temperature. The microstructure of as-deposited and oxidized Tl–Ba–Ca–Cu alloy films was observed using a CCTV attachment to Metzer optical microscope (500 ×) under reflection mode.

X-ray diffraction data were obtained on a microcomputer-controlled Phillips PW-1710 diffractometer

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using CuKα radiation. A standard four-point probe method was used to study the relation between resistivity and temperature. The electrical contacts to the sample were made with a conducting silver paint. The sample was cooled using an APD close cycle refrigerator (model HC-2D). A constant current was passed through the current contacts and the voltage developed was sensed with an eight and half digit precision nanovoltmeter (model 7081). The temperature was recorded using a calibrated silicon diode sensor located close to the sample.

3. Results and discussion

The primary factor that determines the composition of an electrodeposited alloy is the deposition potential of the metals. Since Tl–Ba–Ca–Cu is a quaternary alloy, alloy formation is a complex process. Therefore, for simultaneous deposition of metals, the deposition potential should be such that the electrode potential of the individual deposits comes close to each other and the resultant alloy deposits obtained were uniform, dense and adherent to the substrates. The deposition potential is estimated by studying the nature of cathodic polarization curve. The cathodic polarization curve for deposition of the Tl–Ba–Ca–Cu alloy onto silver substrate is shown in figure 1. The curve was taken at room temperature. The deposition potential for good quality films was – 1·25 V with respect to SCE electrode (– 1·25 V vs SCE). The thickness of the best film for a deposition period of 12 min was of the order of two micron. Figure 2 shows the variation of cathodic current density with deposition time. It has been observed that current density decreases within the first few seconds probably due to the formation of a double layer at the electrode–electrolyte interface causing an increase in surface resistance. It is further noted that the current in the electrolytic deposition cell increases slightly with deposition time. This is attributed to the decrease in resultant resistance of the electrolytic deposition cell due to an increase in the thickness of the film on the electrode material. It is well known that the resistance of the thinner film is higher than the bulk film. As time increases, the film thickness increases and resistance decreases giving rise to an increase in cell current.

The alloyed Tl–Ba–Ca–Cu thin films were then oxidized in oxygen atmosphere in a furnace at 850°C for 50 min. The X-ray diffraction (XRD) pattern of the superconducting Tl–Ba–Ca–Cu–O thin film (figure 3) shows that they contained mainly (2223) phase. The sample showed no dominant impurity phase in the XRD pattern and was shown to be nearly single-phase. Diffraction peaks from silver substrate are also observed in the pattern. The major diffraction lines were indexed with tetragonal indices. The lattice parameter *c* calculated from

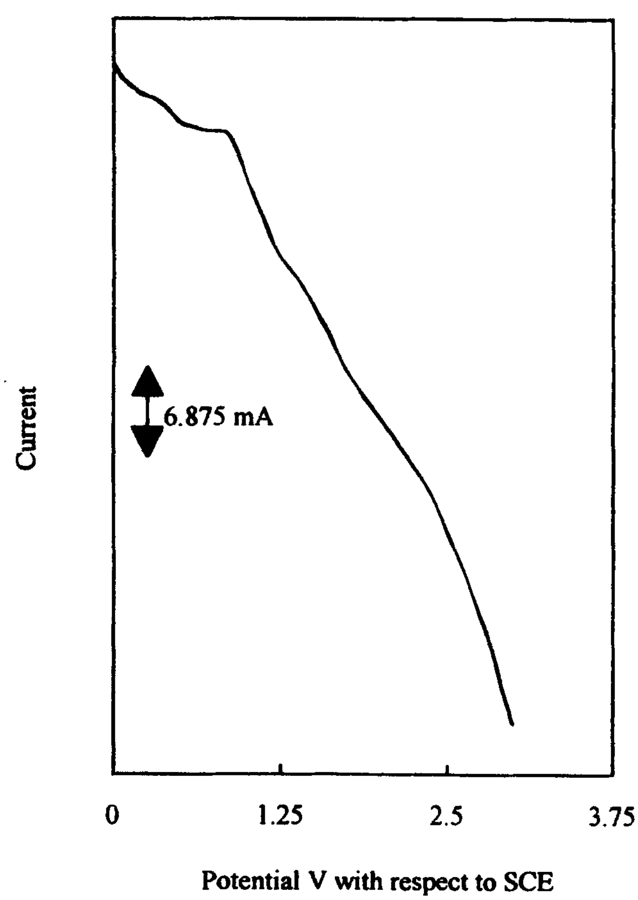

Figure 1. Cathodic polarization curve for the Tl–Ba–Ca–Cu alloy deposition.

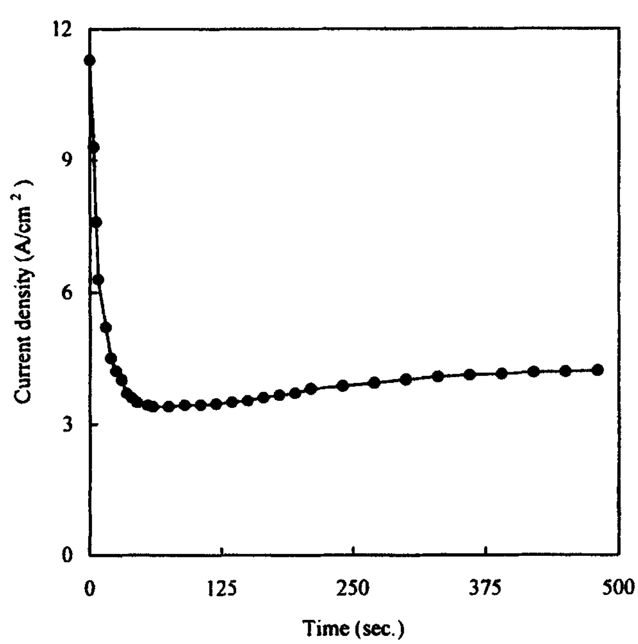

Figure 2. Variation of current density with deposition period during the Tl–Ba–Ca–Cu alloy deposition at – 1·25 V with respect to SCE electrode.

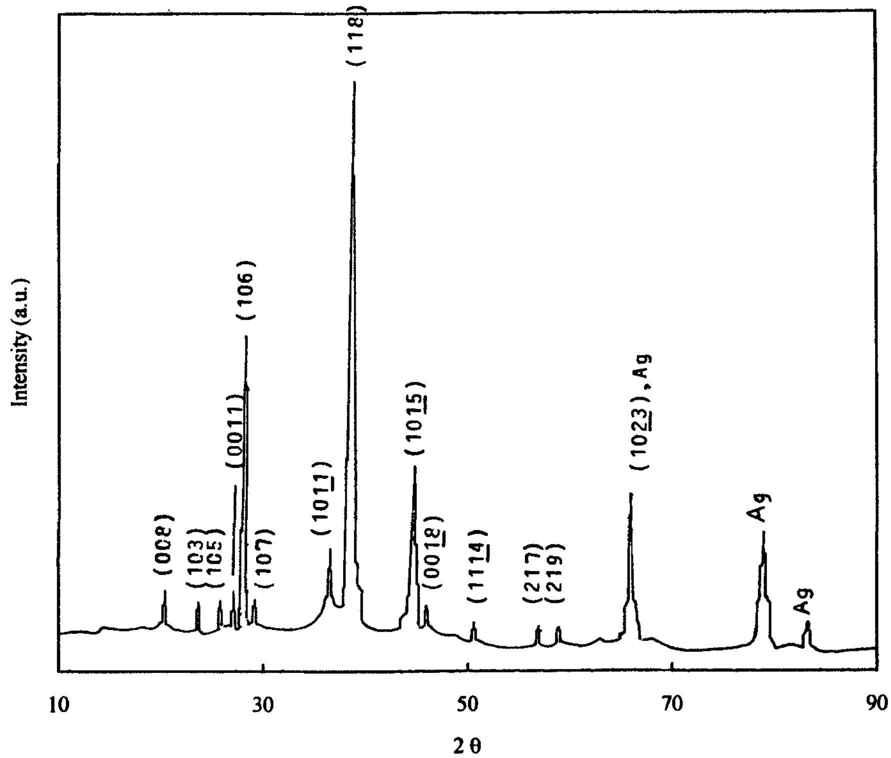

Figure 3. X-ray diffraction pattern of Tl–Ba–Ca–Cu–O films.

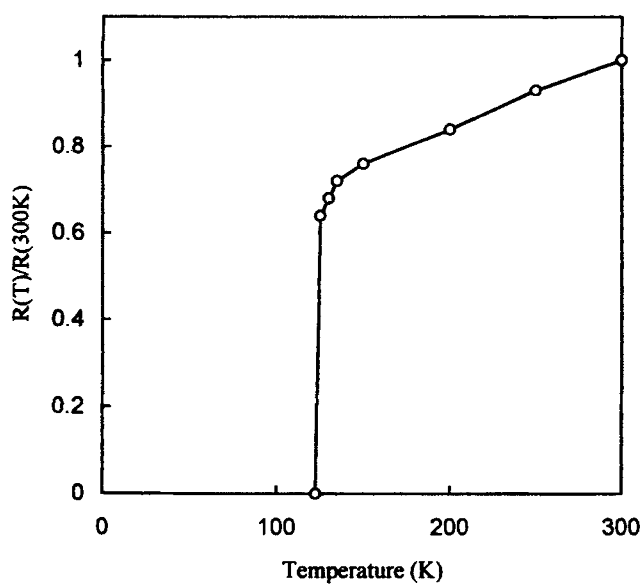

Figure 4. Temperature dependence of the resistivity of Tl–Ba–Ca–Cu–O thin films.

the observed d spacings of the diffraction lines is 35·6 Å and agrees with the c value reported earlier. A standard four-point probe method with a constant current was used to determine the superconducting transition temperature. The temperature dependence of the resistivity of the Tl-(2223) film is shown in figure 4. The sample showed a sharp superconducting transition with T_c onset at about 125 K and superconductivity below 122·5 K.

Annealing at high temperature results in loss of thallium and its oxides. The rate of Tl loss increases with increase of annealing temperature and time. Liu *et al* (1991) proposed that any Tl loss during annealing would create cation vacancies and subsequently increase the hole concentration in the 2223 phase. The proposed increase in hole concentration may be responsible for an increase in T_c. However, higher annealing temperatures facilitate the formation of non-superconducting impurities. Tsai *et al* (1992) suggest that the highest T_c occurs at some intermediate Tl loss. The electrodeposited films annealed at 850°C showed a sharp superconducting transition with $T_{c\,zero}$ = 122·5 K. Since it is possible that the loss of Tl may be evenly compensated by oxygenation, it is difficult to measure the actual loss of Tl during annealing. However, the higher superconducting transition with a sharp transition and absence of any impurity phases in the XRD pattern suggest that the rate of Tl loss is small.

We have also measured the critical current density (J_c) of the Tl–Ba–Ca–CuO thin film following 1 μV/cm electric field criterion. J_c has been found to be $1{\cdot}5 \times 10^3$ A/cm^2 at 77 K and this small value may be due to the weak link behaviour among superconducting grains.

Surface morphology of the as-deposited and oxidized Tl–Ba–Ca–Cu alloy films was studied using optical microscope with a CCTV attachment. The films obtained by the electrodeposition technique were smooth, uniform and dense. The oxidized Tl–Ba–Ca–CuO films showed compact grain structure with reduced intergrain spacing and improved grain size.

4. Conclusion

The Tl-(2223) thin films with better electrical properties have been successfully synthesized using an electrodeposition technique which requires lower annealing temperature, thus reducing the rate of Tl loss. The electrodeposited Tl-thin films showed sharp transition and superconductivity below 122·5 K. Electrical behaviour and XRD data of the electrodeposited Tl-(2223) thin films indicate the existence of single-phase. Electrodeposition is thus a promising technique and provides a better control of stoichiometry and homogeneity of phases.

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