Bull. Mater. Sci., Vol. 24, No. 6, December 2001, pp. 595–601.

Observation of curious spiral growth features in Tl doped Hg bearing high temperature superconducting tapes

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MS received 29 March 2001

Abstract. Synthesis of Hg(Tl)$Ba_2Ca_2Cu_3O_{8+d}$ superconducting tapes have been accomplished by annealing the precursor tape, $Ba_2Ca_2Cu_3O_y$ (fabricated by doctor blade tape casting technique) in an environment of Hg(Tl) vapour. Characterization of superconducting HTSC tape sample was carried out through XRD, TEM, SEM and R–T measurements. Surface morphological investigations of the as-synthesized Hg(Tl)$Ba_2Ca_2Cu_3O_{8+d}$ HTSC tapes by scanning electron microscope have shown the occurrence of curious growth characteristics resembling spiral like features. These growth spirals encompass nearly the whole grain suggesting that spiral growth led to the formation of small crystal like grains of superconducting material Hg(Tl)$Ba_2Ca_2Cu_3O_{8+d}$. The likely mechanism for the generation of these screw dislocations has been elucidated in terms of incoherent coalescence of growth fronts formed from Hg(Tl):1223 and Hg(Tl):1234 nuclei.

Keywords. **Tapes; doctor blade process; spiral growth.**

1. Introduction

Large scale application of superconductors will require wires and tapes with high critical current density J_c, sustainable at high magnetic field. It is known that weak links in polycrystalline sample degrade the value of J_c and result in a rapid decrease in critical current density in the presence of magnetic field due to creeping of magnetic flux line, leading to large thermal decay of current. At high magnetic fields either intergranular weak links effects (Tkaczyk *et al* 1992; Bulaevskii *et al* 1993; Li *et al* 1995; Sun *et al* 1995a, b) or intragranular flux creep (Paasi *et al* 1994; Edelman *et al* 1997) becomes the main J_c controlling mechanism, therefore, better connectivity and stronger flux pinning can make J_c of the tape significantly high and these can be achieved by controlling the microstructure of the specimen. The electrical characteristics (in particular the critical current density) of these cuprate superconductors are sensitive to their underlying microstructure due to their extremely short coherence lengths (typically 15–20 Å), e.g. the critical current density in the bulk form of superconductor, which is highly misaligned is barely of the order of 10^3 A/cm^2 (Burns 1994), on the other hand, in epitaxial thin films or even in *c*-axis oriented polycrystalline films the critical current density lies in the range 10^5–10^7 A/cm^2 (Bourdillon and Bourdillon 1994; Kumar *et al* 1995; Jergel *et al* 1996; Goyal *et al* 1997; Seigel *et al* 1997). A significant improvement in the superconducting properties of both bulk and thin film form of superconductors have been brought about by several workers through greater understanding and control of their microstructural characteristics (Proc. of 3rd international symposium on superconductivity 1991).

It is expected that the control of the density of pinning sites, specifically dislocations, will be important for device application of the high T_c cuprates. In particular this may be vital for highly anisotropic high T_c cuprates containing Bi and Tl, since studies which considered solely point defect pinning sites concluded that these materials will not be useful for applications in high magnetic fields at 77 K. However, linear defects such as screw dislocations, capable of pinning a vortex along a substantial part of its length may extend the temperature and magnetic field range in which these high T_c cuprates may be utilized.

The microstructural investigations employing STM of sputtered (Gerber *et al* 1991; Howley *et al* 1991; Schlom *et al* 1992) and laser ablated (Krebs *et al* 1991; Lang *et al* 1992a, b; Aindow and Yeadon 1994; Sun *et al* 1995a, b) $YBa_2Cu_3O_{7-d}$ films have revealed the presence of high density of screw dislocation (~ 10^9/cm^2) which in addition to having dramatic effect on film formation (spiral growth) are also thought to act as strong vortex pinning sites. Recently, Dam *et al* (1998) has observed a growth mode transition in pulsed laser deposited (PLD) $YBa_2Cu_3O_{7-d}$ films. It is reported that by increasing the background oxygen pressure, the generally observed 2D nucleation and growth mode transforms into a spiral growth. This growth mode transition has been attributed to a change in surface diffusivity of ~ 2 orders of magnitude.

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Here we report on the observation of curious spiral like growth features for the case of Tl doped Hg bearing cuprate high temperature superconducting tapes, prepared through annealing of precursor tape (fabricated by doctor blade process) in an environment of Hg(Tl) vapour. The observations discussed in this paper on the basis of elaborate investigation of the specimen by TEM and SEM, have revealed that growth of superconducting tapes under the present investigations is expected to proceed through screw dislocation mediated spiral growth mechanism.

2. Experimental

Hg(Tl) HTSC tape sample was synthesized by following a two-step process, the first step comprised of the fabrication of $Ba_2Ca_2Cu_3O_y$ precursor tape by doctor blade tape casting technique and the second crucial step involved the reaction of Hg and Tl free precursor by annealing them with an unreacted Hg(Tl)–Ba–Ca–Cu–O pellet in an evacuated (10^{-5} torr) quartz tube.

For synthesizing precursor (Ba–Ca–Cu–O) tape by the doctor blade process, the powders were thoroughly mixed with organic formulation consisting of solvent (ethyl alcohol and trichloroethylene), binder (polyvinyl butyral) plasticizer (polyethylene glycol + octyl pthalate) and wetting agent (fish oil) to form a viscous slip. The viscous slip was then cast under a doctor blade onto the carrier sheet (cellulose film), producing green tape ~ 100 m long × ~ 10 mm wide × ~ 0·5 mm thick. Small tapes 3 mm in width cut from the doctor blade processed green tape were subjected to heat treatment at 500°C for 10 h to remove the organic compounds and after this without any interruption, heat treated at a temperature between 850°C and 890°C for 15–20 h in order to obtain a textured microstructure. As a final step in the preparation of Hg(Tl) tape, the precursor tape together with an unreacted pellet of $Hg_{1-x}Tl_xBa_2Ca_2Cu_3O_{8+d}$ (x = 0·2), was placed in a platinum box (1·3 cm × 0·7 cm × 0·6 cm), which was then tightly closed and put in a quartz tube and sealed. The sealed quartz tube was then kept in a steel tube for safety and inserted in a preheated Heraus furnace at 650°C. To optimize the final processing condition, several runs of annealing treatment were made by varying the annealing temperature and the time span of annealing. Our best result corresponds to annealing parameters: temperature ~ 870°C and time period ~ 16 h. The final Hg(Tl)–Ba–Ca–Cu–O tapes were found to possess typical thickness of 0·5 mm. In the present study the experimental conditions are slightly different from our previous study (Asthana and Srivastava 1997). Here we have taken Cu rich precursor powder with nominal composition $Ba_2Ca_2Cu_{3\cdot2}$ and an attempt has been made to control the Hg pressure in the sealed tube by varying the HgO : precursor ratio in the unreacted pellet of Hg(Tl)–Ba–Ca–Cu–O. The optimum ratio was found to be 1 : 0·2.

The gross phase identification of the as-synthesized Hg(Tl)–HTSC tapes was achieved by recording X-ray diffraction data using a Philips PW1710 diffractometer with CuK_a radiation (20 mA, 30 KV) at a scanning rate of 0·05°/s with scanning angles (2q) in the range 5–70°. The microstructural characterization was accomplished by employing a computerized Philips electron microscope (EM-CM-12) utilizing TEM. The surface microstructural characteristics were monitored through a Philips XL SEM utilizing secondary electrons. The resistance–temperature behaviour was determined by standard four-probe technique. The d.c. transport critical current density was measured across a 1 mm wide bridge using 1 μV/cm criterion.

3. Results and discussion

Gross phase identification of the sample by X-ray revealed the polycrystalline nature of the sample. Analysis of the XRD pattern (figure 1) indicated that the tape samples having the composition $Hg_{0\cdot8}Tl_{0\cdot2}Ba_2Ca_2Cu_3O_{8+d}$

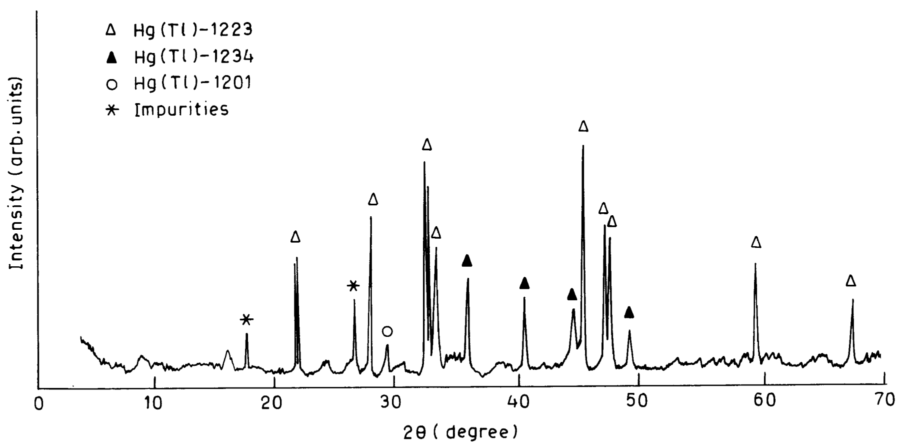

Figure 1. XRD patterns of Hg(Tl):1223 HTSC tapes having composition $Hg_{0\cdot8}Tl_{0\cdot2}Ba_2Ca_2Cu_3O_{8+d}$.

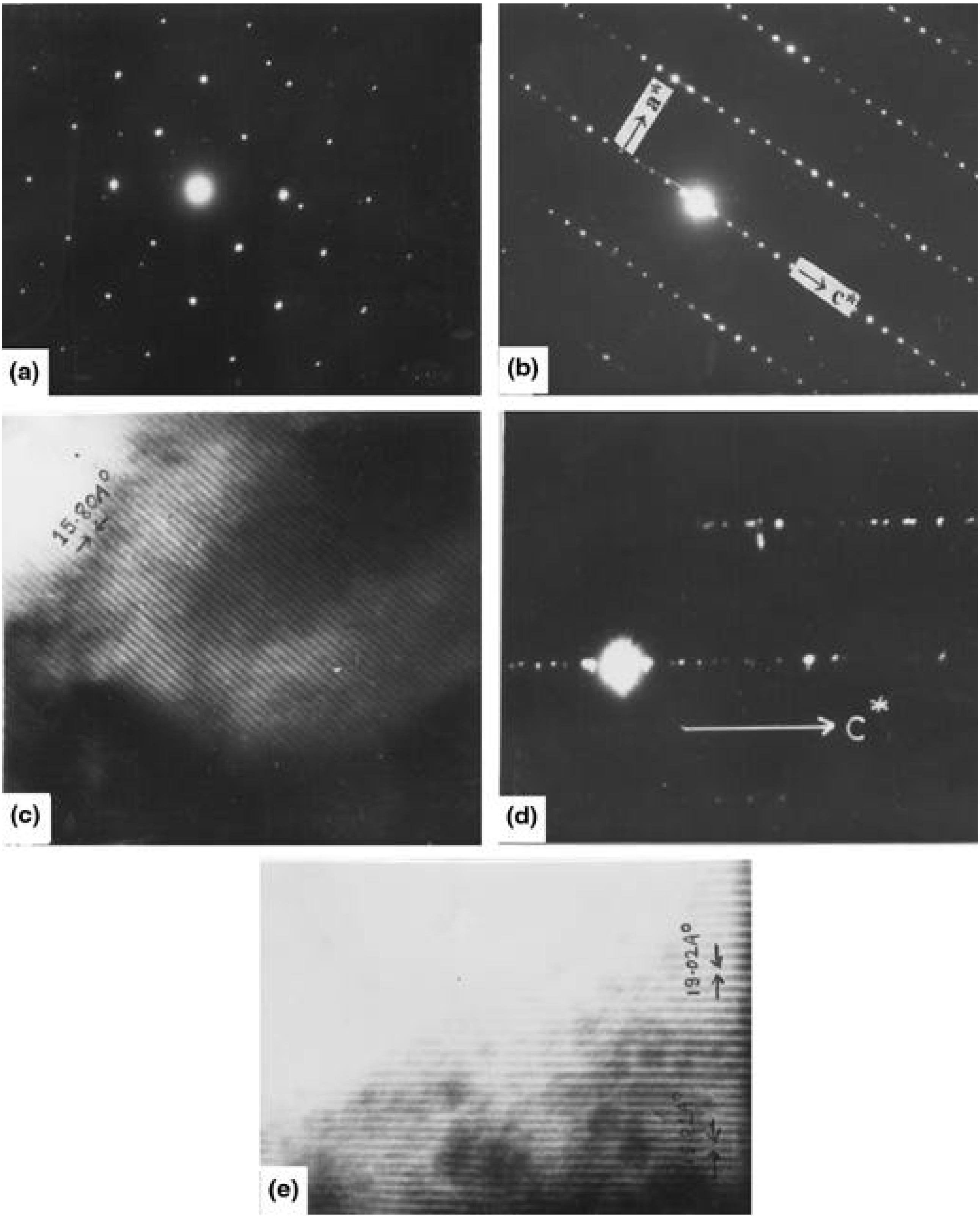

Figure 2. (**a**) [001] selected area electron diffraction (SAD) pattern revealing the tetragonal structure with $a = b = 3{\cdot}85$ Å, (**b**) SAD pattern exhibiting the $a^* - c^*$ reciprocal lattice section of Hg(Tl):1223 phases, (**c**) corresponding high resolution electron micrograph showing the lattice periodicity, $c = 15{\cdot}81$ Å, (**d**) SAD pattern of Hg(Tl) HTSC tapes showing the presence of both Hg(Tl):1223 and Hg(Tl):1234 tetragonal phase and (**e**) corresponding high resolution electron micrograph revealing two types of periodicities i.e. 15·81 Å and 19·02 Å for tetragonal Hg(Tl):1223 and Hg(Tl):1234 phases.

are biphasic with tetragonal 1223 as the majority phase and 1234 as the minority phase which corresponded to the lattice parameter, $a = 3{\cdot}84$ Å and $c = 15{\cdot}78$ Å. Some peaks of impurity phase such as $CaHgO_2$ have also been observed. Results of the X-ray analysis were verified by exploring various samples under transmission electron microscope. Figure 2a represents the [001] selected area electron diffraction (SAD) pattern of Hg(Tl):1223 tape showing the basal plane. Figure 2b brings out a representative SAD pattern of as-synthesized Hg(Tl):1223 tape sample depicting the a^*–c^* direction and figure 2c represents the corresponding high resolution electron micrograph of as-synthesized Hg(Tl) HTSC tape samples. Analysis of these patterns revealed the presence of 1223 tetragonal phase with $a = b = 3{\cdot}85$ Å and $c = 15{\cdot}80$ Å. Some TEM micrographs also show the presence of both Hg(Tl):1223 and Hg(Tl):1234 tetragonal phase as depicted through SAD pattern of figure 2d and corresponding high resolution electron micrograph of figure 2e. Analysis of these patterns show the presence of Hg(Tl):1223 tetragonal phase along with the higher periodicity phase Hg(Tl):1234 having lattice parameter $a = b = 3{\cdot}85$ Å and $c = 19{\cdot}02$ Å.

The resistance vs temperature behaviour (figure 3) of the as-synthesized Hg(Tl) HTSC tape sample shows that the superconducting transition occurs at the temperature of ~ 122 K. The transport critical current density for the tape sample having the composition $Hg_{0{\cdot}8}Tl_{0{\cdot}2}Ba_2Ca_2Cu_3O_{8+d}$ was estimated to be ~ $7{\cdot}25 \times 10^4$ A/cm^2 (20 K).

Surface morphological investigation of the as-synthesized Hg(Tl) tapes by scanning electron microscopy revealed the presence of curious growth characteristics resembling spiral like features. These closed loop growth spirals embedded in the grains of Hg(Tl) tape samples have been observed invariably in all the as-synthesized and processed $Hg(Tl)Ba_2Ca_2Cu_3O_{8+d}$ superconducting tapes. The spiral like features exhibited varied details. As for example, both the circular and polyhedral spiral features (figures 4a, b) from fast and slow growth kinetics reportedly have been observed. These growth spirals lead to the formation of single crystal like grains of superconducting phase Hg(Tl):1223. This grain growth resembles that obtained in superconducting thin films formed through pseudoepitaxy, by deposition on a nearly lattice matched substrate such as $ZrO_2/SrTiO_3/MgO$. SEM micrograph of figure 4c elucidates an example where source of spiral growth has been observed. Figure 4d shows a tower like stepped features on which two sources of spiral growth are seen. According to screw dislocation mediated growth mechanism, it is expected that pairs of screw dislocation of opposite sign in close proximity generate circular atomic steps during growth, the stacking of which forms a tower like feature. SEM micrograph shown in figure 4d is such a kind of growth pattern.

It will be worthwhile to check whether some basic requirements for the formation/growth through spiral are satisfied. We will do this through a calculation of diffusion constant, D and checking its value with the magnitudes known for the growth to be controlled through spiral formation and propagation.

One of the necessary requirements for spiral growth mechanism is that the atomic or molecular species must diffuse into the surface of the crystal and the diffusion length should be larger than the interatomic distance. The estimate of the diffusion coefficient, D based on growth parameter would, therefore reflect on applicability of spiral growth mechanism. According to the screw dislocation mediated theory (Durig *et al* 1984) the diffusion coefficient, D is given by

$$D \approx \frac{K_B T_{\text{growth}} n_{\text{growth}} d^2}{17{\cdot}2 g h a_{\text{jump}}^2},$$

where K_B is the Boltzmann constant, T_{growth} the growth temperature, n_{growth} the macroscopic growth rate, g the surface energy per unit area at the step edge, h the step height, d the distance between successive turns of a growth spiral, and $a_{\text{jump}} \sim (a, b, c)^{1/3}$, is the diffusion jump length, a, b, c are the lattice parameters. Inserting the values $T_{\text{growth}} = 1143$ K, $n_{\text{growth}} = 0{\cdot}1$ nm/sec $d \sim 500$ nm, $g^{[100]} \sim 1{\cdot}6$ J/m^2, $h = 1{\cdot}61$ and $a_{\text{jump}} = (a, b, c)^{1/3} \approx (0{\cdot}385 \times 0{\cdot}385 \times 1{\cdot}58)^{1/3}$ nm into (1), yields $D = 2{\cdot}3 \times 10^{-16}$ cm^{-2}/sec for the $Hg(Tl)Ba_2Ca_2Cu_3O_{8+d}$ tapes. This is in good agreement with the observed value of D for $YBa_2Cu_3O_{7-d}$ HTSC films exhibiting spiral growth features (Howley *et al* 1991). This is suggestive of the fact that the spiral growth mechanism may be operative

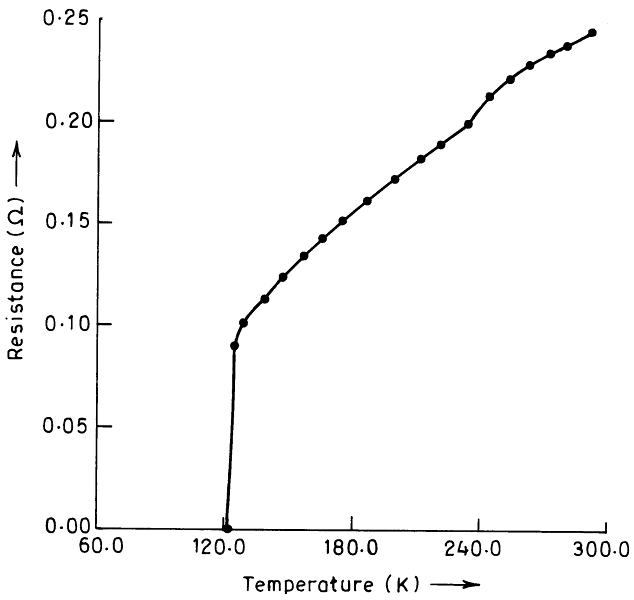

Figure 3. Resistance vs temperature behaviour of the as-synthesized Hg(Tl) HTSC tapes.

in the present investigation on the development of Hg(Tl)BaCaCuO HTSC tapes.

In the present study we have observed both circular and polyhedral types of spiral features. Spirals with circular symmetry are generated when the conditions are such that the distance between the kinks (the reentrant corner where the spiral step shifts through one lattice spacing) or the exchange sites is small and the mean distance of displacement of adsorbed molecule is large, the molecules will have high probability of adhering to the step, if adsorbed near it, irrespective of the orientation of the step. Polyhedral type of spiral features results when the kinks are few and far between and the distance moved by the adsorbed atom is small, the edges of growth steps becoming straight in direction at right angles to the direction of minimum rate of growth (Verma and Krishna 1966).

Several mechanisms have been proposed for the generation of spiral features in the laser ablated and d.c. sputtered $YBa_2Cu_3O_{7-d}$ HTSC films (Gerber *et al* 1991; Howley *et al* 1991; Krebs *et al* 1991; Schlom *et al* 1992; Lang *et al* 1992a, b; Aindow and Yeadon 1994; Sun *et al* 1995a, b). The possible mechanism through which screw dislocation can be created in Y:123 are (i) inheritance (copying) from the substrate, (ii) generation by the formation of dislocation half loops or (iii) incoherent meeting of growth fronts. The observations discussed in this paper are compatible with a screw dislocation generation mechanism involving the incoherent coalescence of growth fronts formed from Hg(Tl):1223 and Hg(Tl):1234 superconducting phases.

Under the present investigations, the precursor tape is already present in the solid form and atoms/molecules of the Hg and Tl in the vapour form are incident on the surface of the precursor material and hit the surface from all sides. Thus when the vapour pressure in contact with the surface of solid precursor is increased above the equilibrium, more and more molecules of Hg(Tl) will join the surface than leave it. In the present case, the adsorbed molecules of Hg(Tl) will diffuse a considerable distance

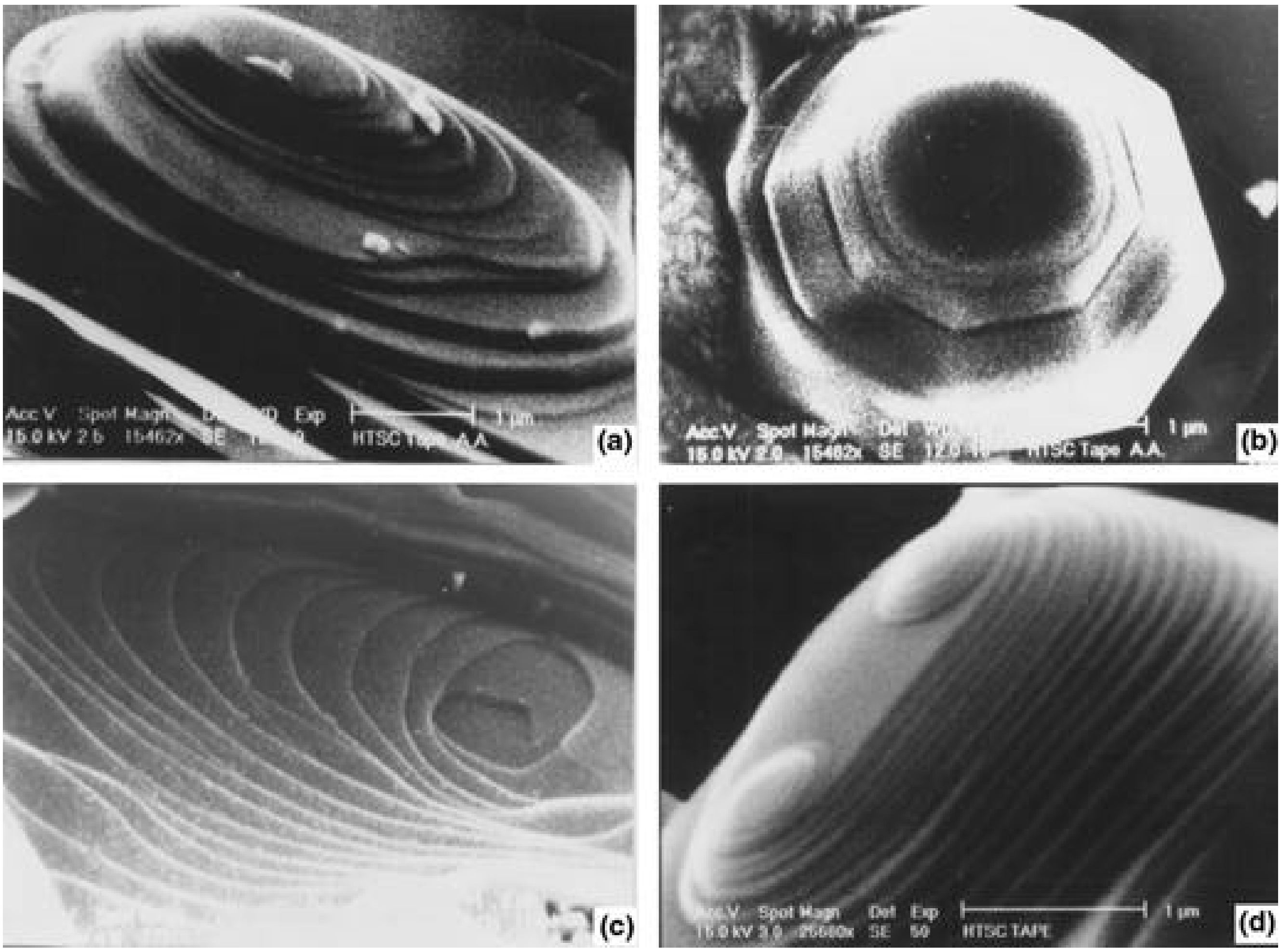

Figure 4. SEM micrograph of Hg(Tl) HTSC tape sample showing (**a**) the spiral growth feature with circular symmetry, (**b**) polyhedra type of spiral features, (**c**) exhibiting the source of spiral like growth features and (**d**) tower like stepped features formed by two oppositely signed screw dislocation.

(of the order of few hundred molecular diameter) into the surface of solid precursor tape, forming the island or patches of Hg(Tl):1223 and Hg(Tl):1234 superconducting phase. When two growth fronts corresponding to Hg(Tl)–1223 and Hg(Tl)–1234 would develop sufficiently and meet each other incoherently, a screw dislocation is expected to form. Since these two phases do not match each other along the *c* direction (*c* periodicity of Hg:1223 (c_2) = 15·81 Å and Hg:1234 (c_1) = 19·02 Å) incoherent meeting of these two growth fronts would create steps/ledges leading to the development of spiral like growth features having steps of height '*h*' as either equal to the difference or integral multiple (*n*) of the difference of their periodicity i.e. $h = c_1 - c_2$ or $h = n\ (c_1 - c_2)$. The basic feature of this is elucidated in figure 6. It is expected that at optimum supersaturation, more and more molecules of Hg(Tl) from vapour of Hg(Tl) would diffuse into the solid precursor either through the surface or through dislocation core, will join the step and convert the precursor into superconducting Hg(Tl)$Ba_2Ca_2Cu_3O_{8+d}$ phase.

It is known that if Burgers vector > 10 Å, the core of dislocation will be hollow (Frank 1951; Cottrell 1953). The Burgers vector which is equivalent to or multiple of lattice parameter is already large in the case of HTSC material along the *c* direction, since the *c* periodicity for Hg-1223 and Hg-1234 phases are 15·81 Å and 19·02 Å. In the present investigation, the core of dislocation of HTSC material (which is a heavily disordered material) may contain high degree of disorder or may be hollow. In either case, it is expected that a fast diffusion of incident atoms may take place. Here the incident atoms are Hg(Tl) atoms and the background precursor phase in which they are incident is highly unstable precursor matrix. In view of the expected fast diffusion as suggested above of Hg(Tl) atoms, it is expected that precursor will get converted/transformed into stable superconducting phase, Hg(Tl):1223 and this transformation-cum-growth will propagate through a screw dislocation mediated spiral growth. This is in keeping with the observed results where spiral growth features have been extensively observed in all the samples studied.

In passing it may be mentioned that the present suggested mechanism appears to be the most plausible one for explaining the screw dislocation mediated growth of large Hg(Tl)–Ba–Ca–Cu–O regions (grains) via formation of spiral like growth features.

Since our precursor tape samples alone (figure 5) do not exhibit such features, these spirals may be taken to

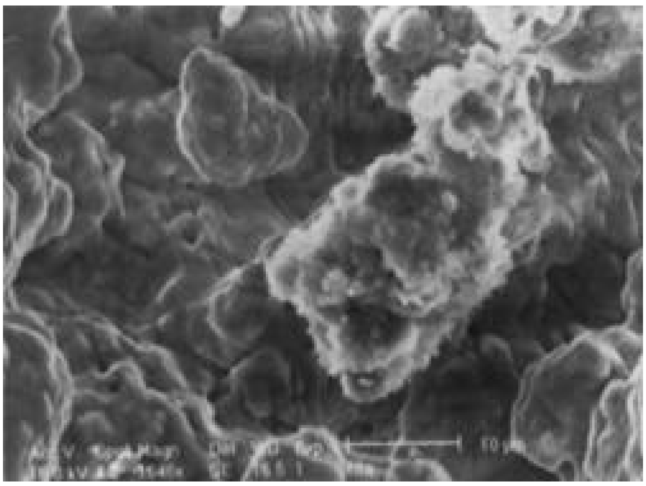

Figure 5. SEM micrograph of the precursor, $Ba_2Ca_2Cu_3O_{8+d}$ tape sample.

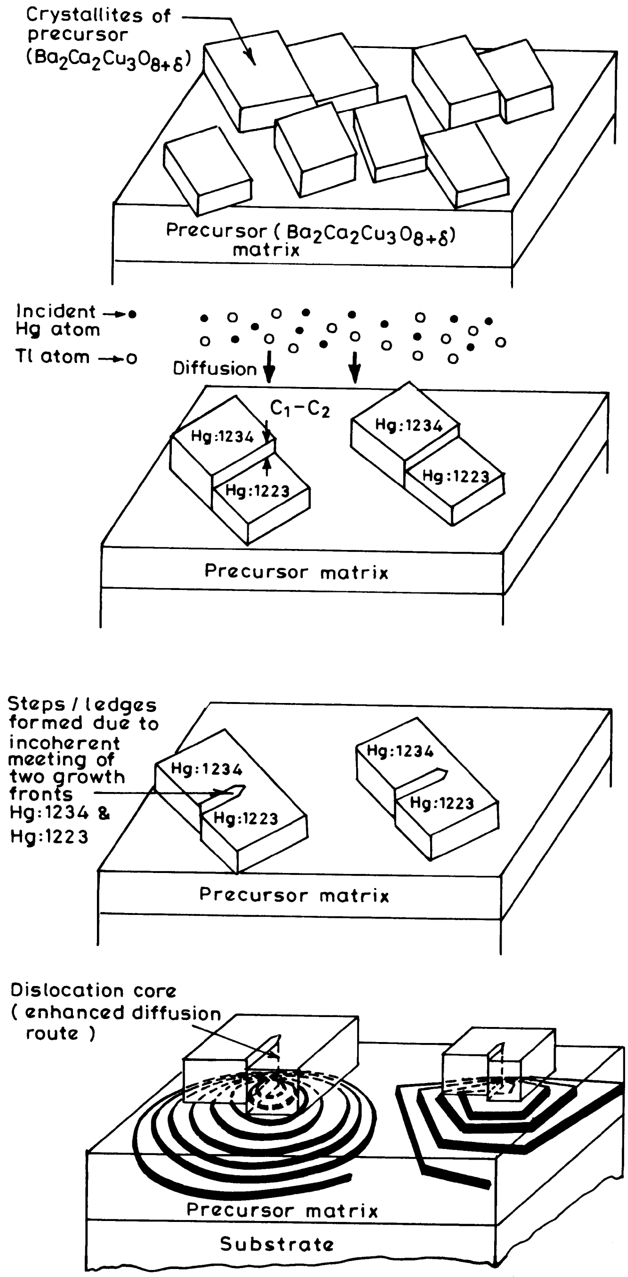

Figure 6. Model showing the schematic representation of the proposed mechanism for spiral growth features.

manifest the growth characteristic of the present Tl doped Hg–Ba–Ca–Cu–O tape. The presence of spiral like growth features in the tape apparently assists in texturing (001) oriented grains as dominant variety. This texturing will lead to the enhancement of critical current density.

4. Conclusions

The observed surface morphology of the as-synthesized Hg(Tl)$Ba_2Ca_2Cu_3O_{8+d}$ HTSC tapes by scanning electron microscopy have elucidated the presence of spiral like growth features. Both circular and polygonal types of spiral features from fast and slow growth kinetics reportedly have been found to occur. The creation of spiral features through screw dislocation mediated growth mechanism, formed from the incoherent meeting of Hg(Tl):1223 and Hg(Tl):1234 superconducting phases has been suggested.

Acknowledgements

The authors are grateful to Prof. A R Verma and Prof. R P Rastogi for encouragement. Thanks are due to A V Narlikar, T V Ramakrishnan, D E Gamelin and H M Hermann for helpful discussions. Financial support from UGC, CSIR and DST is also gratefully acknowledged.

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