Shock wave synthesis and processing of high temperature superconductors with defect microstructures

Z IQBAL*, N N THADHANI[#], K V RAO⁺, R PUZNIAK⁺,
R SHARMA^{**}, B L RAMAKRISHNA^{**}, H ECKHARDT* and
F J OWENS⁺⁺

*Allied-Signal Inc., Corporate Technology, Morristown NJ 07962, USA

[#]CETR, New Mexico Institute of Mining and Technology, Socorro NM 87801, USA

⁺Department of Solid State Physics, Royal Institute of Technology, Stockholm, Sweden

^{**}Department of Chemistry and Center for Solid State Science, Arizona State University, Tempe AZ 85287, USA

⁺⁺Department of Physics, Hunter College, City University of New York, New York 10011, USA, and ARDEC, Picatinny NJ 07801, USA

Abstract. The tetragonal ($T_c = 55$ K) and orthorhombic (non-superconducting) $Tl_2Ba_2CuO_6$ (Tl 2201) phases have been synthesized by a *ca* 20 GPa planar shock wave in a microsecond time frame. Because of local rapid quench rates (up to 10^6 K/s) defects related to metastable phases are frozen in the sample. In the 2201 phase the predominant defect identified by high resolution lattice imaging corresponds to a Tl–Ba–Cu–Tl–Cu (Tl 1212) phase which is metastable but can be synthesized via a low temperature reaction. Defects of this type may account for the enhanced flux trapping observed in the material using field modulated microwave absorption. Attempts at shock synthesizing the more complex $Tl_2Ba_2CaCu_2O_8$ and $Tl_2Ba_2Ca_2Cu_3O_{10}$ phases are also discussed. Shock processing pre-synthesized $YBa_2Cu_3O_7$ powder in the radial geometry followed by an O_2 anneal at 890 °C produces near-theoretical density cylinders that sustain inter-grain critical currents at zero field of 1350 and 750 amps/cm² at 60 and 77 K respectively. The magnetic field dependence of the critical current and the magnitude of flux-pinning in this material relative to sintered pellets are enhanced by a factor of 2–3. Preliminary investigations of the defect microstructure of this material are discussed.

Keywords. Shock wave synthesis; superconductors; defect microstructures.

1. Introduction

We have been studying the application of shock waves in different geometries and pressure ranges as a method of producing highly dense bulk superconductors with well-defined defects which can act as flux pinning centers (Iqbal 1988; Iqbal *et al* 1989a,b). Related work using a variety of experimental arrangements has been carried out by other groups in USA, Japan and USSR (Morosin *et al* 1989 and references therein; Murr *et al* 1989; Syono *et al* 1989; Nesterenko 1989). Shock waves produced in a gas gun or in an explosive detonation front provide dynamic pressures ranging from 1 to 100 GPa with durations of a few microseconds. Local temperatures in the solid can rise by a few thousand degrees as indicated by two-dimensional simulations for different packing densities (Thadhani 1988). This is followed by extremely fast quench rates of up to 10^6 K/s which allows the fabrication of metastable or non-equilibrium structures.

In this paper we will discuss experiments carried out in the 10 to 25 GPa regime aimed at shock-synthesizing the Tl-based superconductors with built-in novel defects. Initial results of some of this work have been reported by Iqbal *et al* (1989b). Previous shock synthesis attempts have been made in the LaSrCuO, YBaCuO and BiSrCaCuO

systems, with sizable conversions to the superconducting phase structure achieved only in the case of the La compound (Morosin *et al* 1989). However, the samples still had to be annealed under O_2 to achieve the correct superconducting stoichiometry. We also report on the shock-induced modification of pre-synthesized $YBa_2Cu_3O_7$ (Y123) powder in the pressure regime below 10 GPa and in a radial geometry. The shock-modified material when O_2 -annealed provided samples with critical-state properties that were improved compared with those of conventionally processed material.

2. Experimental aspects

The set-up used for the synthesis experiments consists of a steel flyer plate which is explosively accelerated over a 10–20 mm stand-off distance and impact powders contained in steel capsules embedded in the cavities of a steel recovery fixture. Impact planarity is achieved via the use of a plane wave shock lens arrangement (Thadhani 1988). The precursor powders were packed at typically ca. 60% of theoretical density and the impact plate is monitored during the experiment by a high speed camera.

The consolidation-modification experiments were performed in a cylindrical geometry which utilizes radial grazing angle shock loading. The precursor powder (packed to ca. 45% density for these experiments) was placed in a thin-walled copper tube (outer diameter of 2.5 cm). The explosive was packed into an outer concentric tube and ignited from the top to set up a cylindrical convergent shock wave that propagates through the powder resulting in near theoretical density consolidation.

The Tl-based precursors for the shock synthesis experiments consisted of finely ground powders of Tl_2O_3 and a matrix material (to which unreacted BaO_2 was added in some experiments). For synthesis of $Tl_2Ba_2CuO_6$ (Tl 2201) phase the matrix material was of nominal composition $Ba_2Cu_3O_x$ which was prepared by firing $BaCO_3$ and CuO at 930 C in air for 30 h. Experiments on the synthesis of the Tl 2201 phase were performed using precursor powders of nominal Tl–Ba–Cu atomic ratios of 1–2–3, 2–2–3 and 2–2–1. The 221 ratio was achieved by adding BaO_2 . Experiments aimed at preparing the $Tl_2Ba_2CaCu_2O_2$ (Tl 2212) and $Tl_2Ba_2Ca_2Cu_3O_{10}$ (Tl 2223) phases used a matrix of composition $Ba_2Ca_2Cu_3O_x$ prepared by firing $BaCO_3$, $CaCO_3$ and CuO at 875 C for 20 h in air. Firing the matrix mixture above 900 C resulted in partial melting and difficulty in obtaining a smoothly mixed precursor powder. Experiments were carried out with precursors of Tl–Ba–Ca–Cu atomic ratios of 1–2–2–3 and 2–2–2–3.

The precursor powder for the shock consolidation-modification experiments was conventionally synthesized Y123 powder of average grain size of 1–5 μm (obtained from Superconductive Components Inc). The powder did not contain impurity phases down to a 1% volume level as checked by X-ray diffraction and (for paramagnetic phases) down to the ppm level as checked by EPR.

3. Synthesis, results and discussion

Shock synthesis of Tl 2201 with $\geq 85\%$ conversion was achieved at pressures approaching 20 GPa using the planar geometry and 123 and 221 precursor powders prepared as described in §2. The X-ray patterns are shown in figure 1. From the patterns it is evident that the near-tetragonal ($c = 23.16 \text{ \AA}$) phase is obtained from

Figure 1. Powder X-ray patterns from shock products obtained from Tl-based precursor compositions indicated on the top corner of each pattern. The numbers labelling the reflections are the hkl indices.

Tl-deficient 123 precursors, whereas the orthorhombic phase was obtained from the stoichiometric 221 precursor. Note that the latter precursor contained BaO_2 and all experiments were performed in a reduced oxygen atmosphere. The product obtained from the 223 precursor showed a large fraction of unconverted Tl_2O_3 and a minority fraction of the Tl 2201 phase. The diffraction patterns indicated the presence of a new phase which will be discussed below. Both the products from 123 and 223 precursors showed superconductivity in the as-synthesized state (figure 2). T_c (zero) values are 55 and 20 K respectively for the 123 and 223 products. Diamagnetic fractions are low for the 223 product but greater than 20% for the Tl-deficient 123 product, which in addition shows a diamagnetic onset at 70 K. Consistent with the work of Hewat *et al* (1988), the orthorhombic phase obtained from the 221 product is not superconducting down to 4 K.

Analytical TEM (transmission electron microscopy) showed the composition of the 221 product to be close to that of the Tl 2201 phase. However, the 123 product microcrystals showed a Tl-Ba-Cu = 2-2-2 composition. It is likely that the excess Cu

Figure 2. Normalized resistivity data (50 mA current) for shock products obtained from Tl-Ba-Cu = 123, 223, 221 and Tl-Ba-Ca-Cu = 2223 precursors.

Figure 3. Peak to peak hysteresis at 70 K (for shock and conventionally synthesized $\text{Tl}_2\text{Ba}_2\text{CuO}_6$) of the magnetic field positions of the non-resonant microwave absorption for decreasing and increasing field scans versus the maximum magnetic field applied to the sample.

is associated with poorly crystallized CuO coating the microcrystals. High resolution lattice imaging of the 123 product reveals intergrowths of the single Tl-layer and non-superconducting $\text{TlBa}_2\text{CuO}_5$ phase, but in addition extensive defects of the type $\text{Ba-Cu}-\square\text{-Cu-Ba}-$ are observed only in the 123 and not in the 221 product. Computer simulations indicate partial Tl-occupancy between the two copper layers of the defect. The defect would correspond to metastable $\text{TlBa}_2\text{TlCu}_2\text{O}_7$ (Tl 1212*). We attempted to synthesize this phase by conventional low temperature firing under O_2 (750 C for 1 h) of a stoichiometric precursor consisting of Tl_2O_3 and BaCuO_2 . Partial formation is observed of a new phase with some X-ray lines corresponding to the unknown phase

pattern of shock synthesized Tl 2201 (figure 1). Under the present synthesis conditions this phase is weakly semiconducting. Further work on this novel phase is in progress.

Estimates of the transport critical current of the 123 product were made via the AC susceptibility method (see below) and found to be low, probably due to sample porosity caused by O and Tl diffusion during the synthesis process. Filling the pores with Ag may be necessary to achieve useful critical current densities. However, the hysteresis of the field position of the non-resonant microwave absorption below T_c , which is related to flux-trapping in the critical state (Owens 1989; Owens and Iqbal 1990) shows an increase for the shock-synthesized Tl 2201 compared with conventionally prepared material, as shown in figure 3 for different maximum applied fields. This suggests that defects of the type discussed above play a role in enhancing the pinning forces.

Synthesis experiments aimed at fabricating the 3 copper oxide layer 125 K phase by the methods discussed above were not entirely successful. The increased multicomponent nature of the precursor powder probably hinders the solid-state reaction processes. An X-ray diffraction pattern of the 2223 product is shown in figure 1. A small fraction of the Tl 2122 phase is indeed formed together with an unknown phase and a large fraction of unreacted Tl_2O_3 . The resistivity data (figure 2) show no indication of superconductivity down to 10 K, indicating that the Tl 2122 phase formed has its oxygen sub-lattice disordered as a result of the shock wave (this is in contrast to the more robust behaviour of the Tl 2201 phase). Similar results are obtained for experiments using the 1223 precursor.

4. Shock consolidation-modification

Shock consolidation-modification experiments were carried out in the cylindrical geometry at 10 GPa using Y123 powder. The as-shocked cylinders ($\geq 90\%$ theoretical density) were machined into bars and annealed in flowing O_2 for 12 h at 890 C followed by an 8 h cool. The resistivity data for these shock-annealed samples showed a drop at 93 K to nominally zero resistance with a transition width of *ca.* 1 K. DC SQUID magnetization data (figure 4a) show 100% shielding at 4 K with a sharp onset at 93 K for an applied field of 20 Oe. Meissner signals are lower by a factor of 8 compared with a factor of 2 decrease for the as-shocked and conventionally sintered precursor powder. Additionally, for the shock + annealed sample the remnant field obtained on turning off the applied DC field corresponds to the zero field moment. All this indicates enhanced flux trapping in the shock + annealed sample. This is also evident in the high-field magnetization hysteresis loops in fields up to 20 kOe, where the hysteresis at 20 kOe for the shock + annealed compared with the as-shocked samples are enhanced by a factor of *ca.* 1.5 (see figure 4b).

Inter-grain critical currents at different temperatures were obtained by two non-contact methods. In the first method the real and imaginary (loss) components of the AC susceptibility at different temperatures below T_c were used as described by Chen *et al* (1989). In the second method (Rao 1989) low DC field (in the vicinity of H_{c1}) hysteretic loops were obtained and J_c 's calculated for fields up to *ca.* 200 Oe using Bean's equation, the slab thickness and the measured hysteresis. Both methods gave nearly the same values of J_c : 3250 amps/cm² at 4 K, 1350 amps/cm² at 60 K and 750 amps/cm² at 77 K in zero field. The value at 77 K is comparable to that reported by Dwir *et al* (1989) for conventionally sintered Y123-Ag composites and a factor of 1.5 to 2 better than

Figure 4. a. Magnetic moment versus temperature at 20 Oe DC field for as-shocked and shock + annealed $\text{YBa}_2\text{Cu}_3\text{O}_7$. FC and ZFC represent field-cooled and zero field-cooled data respectively. b. Magnetic moment versus field hysteresis loops for the two samples above at 4 K.

Figure 5. Normalized transport J_c at 4.2 K for shock + annealed and conventionally-sintered $\text{YBa}_2\text{Cu}_3\text{O}_7$.

Figure 6. Transmission electron micrograph of shock + annealed YBa₂Cu₃O₇ microcrystal together with the corresponding 001 setting electron diffraction pattern.

typical sintered Y123. The J_c values at zero field normalized to the values at higher fields at 4 K for the shock + annealed and sintered samples are plotted in figure 5 for DC fields up to ca. 120 Oe. It is evident that the drop off with field is much lower for the shock + annealed sample and J_c is a factor of 3 higher at 100 Oe. This is consistent with the data showing enhanced flux trapping and suggests that coupled with grain orientation the shock method may provide J_c 's approaching those of melt textured material.

We have also examined the microstructure of the shock + annealed samples in some detail. X-ray diffraction shows a small decrease in the orthorhombic splitting and a shoulder appears near 80 K in susceptibility data taken at fields near 30 Oe. This suggests the existence of a metastable O-sublattice or Y at Ba sites (Iqbal *et al* 1988) which might actually degrade bulk transport J_c in our material at 77 K. In addition TEM shows the existence of a large number of microcrystals with interpenetrating twins and dislocations as is evident in figure 6. The electron diffraction pattern shows no indication of superlattice reflections. Comparison with as-shocked material shows a clear-cut growth of interpenetrating twins on annealing. It is likely that the annealing step releases shock-induced strain via the formation of the microstructure shown in figure 6 which provides the sites for flux pinning. These sites may also be the seat of atomic scale defects which are being studied by lattice imaging techniques.

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