

## ISTEC-MRS Workshop Covers Materials Processing and Applications of High $T_c$ Superconductors

An international workshop on Suitable Materials and Processing for HTS Applications: Towards the Next Decade was held at the Royal Waikoloan, Big Island, Hawaii, on June 15–18, 1997. The workshop was co-sponsored by the International Superconductivity Technology Center (ISTEC) of Japan and the Materials Research Society. Progress in processing and properties made over the past ten years since the discovery of oxide superconductors could be readily assessed by talks and posters at this year's workshop.

The goals of the 1997 Workshop were recognized implicitly from the session topics: crystal growth related to HTS processing of bulk and films; processing of HTS wire, tapes, and thick films; ac losses, vortex dynamics, and pinning; thin film processing for radio frequency (rf) applications; processing of HTS bulk; and fabrication and control of HTS junctions and applications. The combination of detailed information and focused audience interest was ideal for promoting exchange among researchers, furthering the drive toward full-scale emergence of high-temperature superconducting technologies.

The workshop was chaired by Shoji Tanaka of ISTEC and Robert Hull of MRS. Financial support was provided by ISTEC, Japan Keirin Association, Argonne National Laboratory (ANL), Los Alamos National Laboratory (LANL), National High Magnetic Field Laboratory (NHMFL), Naval Research Laboratory (NRL), Oak Ridge National Laboratory (ORNL), Science and Technology Center for Superconductivity at the University of Illinois at Urbana-Champaign, and Texas Center for Superconductivity at the University of Houston (TCSUH). The four-day program saw 150 attendees from 14 countries. In addition to three days of 72 oral presentations, approximately 60 posters were presented.

The technical program began with an opening ceremony and two special plenary lectures, followed by a series of plenary talks. In the special lectures, Tanaka (SRL-ISTEC) talked about the expectation of future superconductivity technology, using electronic device applications as an example. He showed the future simulation indicating that most of the present technologies including semiconductors, supercomputers, magnetic and optical memory devices, and optical networks may reach critical points around the year 2005, and concluded with the need to establish superconducting device technol-

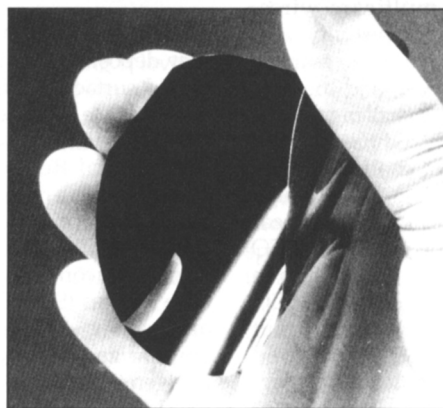
ogy by that year due to its advantages of very high speed, low power consumption, easiness of the system image, and not impossible fabrication processes. D.C. Larbalestier (University of Wisconsin—Madison) lectured on materials challenges for superconducting applications, especially focusing on BSCCO tape processing and its current density ( $J_c$ ) properties. He showed the influence of many factors that

produce barriers to current flow. These barriers lead to the overall  $J_c$  being very much less than the true local  $J_c$ —as little as 10% of the local value. This conclusion was confirmed by experimental tests of single filaments taken from very high  $J_c$  multifilament composites.

A series of plenary talks followed. K. Tanabe (SRL-ISTEC) reviewed the structure of some superconducting systems and

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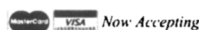
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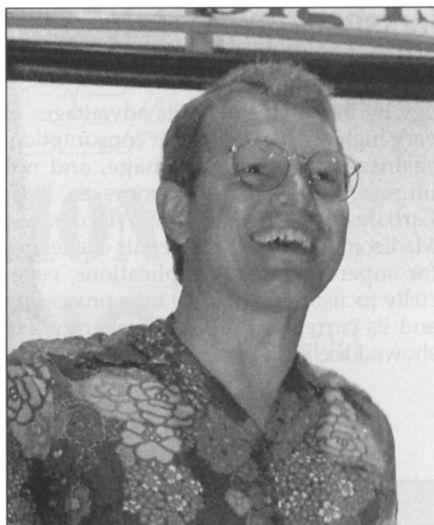
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talked about methods to increase  $T_c$  in Tl and Hg superconductive compounds. He noted that Tl and Hg conductors have higher  $T_c$  under applied pressures and reiterated that one method to increase  $T_c$  would be to incorporate structural changes in the 1 atm crystal structure that occur at elevated pressure by chemical means. He reviewed his latest work on two-step processing of Hg-1223 films. R. Flukiger (University of Geneva) talked about fabricating Bi-2223 tapes. His group is using a four-roll system with driven vertical and horizontal rolls. The advantage of this system is that each filament in a multifilamentary wire has nearly the same deformation state. His group has also introduced cross-filament and tilted filament stackings to alleviate anisotropy problems in Bi-2223 tapes. Flukiger said they are using BaZrO<sub>3</sub> as a barrier material between each Ag-clad internal filament to decouple the filaments and reduce ac losses. H. Yamasaki (ETL, Japan) reviewed recent progress in HTS wire fabrication and applications. He indicated that the reduction of ac losses is the key for power device applications. For this purpose twisting the multicore wires, increasing the Ag matrix resistivity, and decreasing core thickness are necessary to reduce both coupling losses and the hysteresis loss, which are the challenge in the next decade. He also introduced the in-plane-aligned YBCO film conductor technology which gives an expectation of high field magnets operated at 77 K in the near future, including his expectation of YBCO thin film tapes having lower ac losses in parallel fields than multicore BSCCO tapes. W.K. Chu (TCSUH) talked about applications that use HTS. He showed three basic building blocks (levitator, magnetic clutch, and vibration damper) that his group uses to design their levitation devices. Chu said that the levitation devices they design at TCSUH do not use the levitation force from the superconductor to lift an object. Rather, the superconductor is placed between two opposite poles of opposing magnets and it stabilizes the repulsive force between the magnets so they do not fly apart. The levitation is due to the mutual repulsion between the two permanent magnets. He showed a recent design for a vibration-free telescope mount for a moon-based telescope. M. Kawasaki (Tokyo Inst. of Tech.) gave an overview of his group's studies to improve the surface roughness of YBCO films. The researchers have developed an etch that leaves the surface of a SrTiO<sub>3</sub> substrate with ledges that are terminated exclusively with Ti-O layers. They found that depositing YBCO on the Ti-O layer leads to precipitates in the YBCO film. In contrast, if



*E. Hellstrom (University of Wisconsin—Madison) co-chaired the program committee for the 1997 International Workshop on Superconductivity held at the Royal Waikoloan, Big Island, Hawaii, on June 15–18, 1997.*

they deposit a single layer of SrO onto the etched surface that is terminated with the Ti-O surface layer, essentially no precipitates form in the YBCO layer. M. Nisenoff (U.S. Naval Research Lab.) discussed materials challenges of using HTS materials in electronic devices. He identified three main categories of thin film applications: semiconducting quantum interference devices (SQUIDS), rf and microwave applications, and digital applications. He emphasized that the advantages for the refrigeration system when using HTS system is balanced by the greater complexity of the HTS materials systems compared to low-temperature superconductors (LTS) thin-film systems. He mentioned the "Big 3" collaboration in the United States between Northrop-Grumman, TRW, and Conductus to work on generic thin film problems. They have been collaborating since 1995, exchanging knowledge and samples. He suggested an international collaboration between the United States, Japan, and Europe to work on precompetitive, generic issues that plague HTS film and device fabrication.

Sessions on crystal growth related to HTS processing of bulk and films followed. Twelve talks were devoted to RE-123, BSCCO, and Hg-oxide superconductors, including thin-film growth, bulk single-crystal growth, and tape conductors. Over the past few years, significant advances have been made in production of large NdBCO single crystals and YBCO-coated

conductors. Recent work on control of composition and phase stability to produce higher  $T_c$  (~96 K) for NdBCO crystals was discussed. Use of low oxygen partial pressure or BaO rich liquid solvent suppresses the substitution of Nd with Ba, resulting in formation of high  $T_c$  stoichiometric 123 NdBCO crystals. The development of YBCO tape conductors was being watched with keen interest. Epitaxial YBCO film growth processes on either biaxially textured Ni metal substrates or biaxially textured YSZ IBAD buffer layers on polycrystalline Ni-superalloy substrates were given attention as the next generation HTS conductors. Single-crystal growth and its superconducting properties of Bi(Pb)-2223 using a fused-salt reaction technique and phase changes and morphology control of Bi-2212 tapes by the continuous heat treatment techniques were also presented. These talks were highly useful in understanding BSCCO tape properties and for further development of tape conductors.

Sessions on processing of HTS wire, tapes, and thick films followed. The first two talks were devoted to YBCO-coated conductors produced by the liquid phase epitaxy (LPE) method, introducing a high production rates of >10  $\mu\text{m}/\text{min}$  and 10- $\mu\text{m}$ -thick conductors with high  $J_c$  of >10<sup>6</sup> A/cm<sup>2</sup>. The researchers reported on decreasing the LPE process temperature by addition of fluorine and silver to the barium cuprate solvent. The third talk was devoted to surface barrier effects in the magnetization of YBCO films. The experimental results show that surface barriers reduce the hysteresis loss in parallel magnetic fields. The talk on the transport  $J_c$  of biaxially oriented Tl-1223 superconductor on textured Ag tapes followed. The presenters introduced results of high  $J_s$  of 10<sup>5</sup> A/cm<sup>2</sup> at 77 K, 0 T and 1.5 10<sup>4</sup> A/cm<sup>2</sup> at 77 K, 1 T. Magnetic properties of HgBCCO epitaxial thick films by the spray pyrolysis technique and the improved flux pinning in Bi-2212 tapes by BaO<sub>2</sub> and MgO addition were also reported. These two talks suggested further possibilities of improvements in  $J_c$  of HTS conductors. The last seven talks were devoted to Bi-2223 wires and three of them were for applications. These presentations recognize that manufacturing of Bi-2223 powder in a tube (PIT) wire had already stepped forward to the industrial stage. Although the magnets need refrigeration, the magnetic fields of 4 T were generated by the solenoid coil. Transmission cable, transformer, and fault current limiter were introduced as good target applications of Bi-2223 wires in the near future. On the contrary, four presentations showed that many unknown and mysterious issues

remained unsolved in formation reactions of Bi-2223. These talks characterized this workshop which had the main theme of processing for HTS application. During the thermomechanical processing of Bi-2223 PIT wires, very complicated reactions occurred which depended on the starting materials and heat treatment patterns. Transmission electron microscopy (TEM) observations indicated that the formation of Bi-2223 was proceeded by both processes of nucleation-growth and intercalation of Ca and Cu into the Bi-2212 phase. It was also reported that the performance of the wire was strongly affected by the microstructure and *c*-axis texture of the Bi-2223 crystals. The *ab* basal plane grain boundary and edge colony boundary were observed in the sample with  $J_c$  value of 55 kA/cm<sup>2</sup>. All investigations indicated that the control of grain boundaries and second phases including Bi-2212 and Bi-2201 were important for further improvement of properties of Bi-2223 wires.

In the session on processing of HTS bulk, the first six talks focused on improving texturing, growth kinetics, second-phase particle dispersion, and superconducting state properties for RE-123 superconductors prepared by the melt-processing method. Results revealed promising methods for increasing the directional solidification rate of Nd-123 by a factor of about 50, for using the 211 phase as an additive to absorb excess liquid during 123 solidification, and for applying melt textured Yb-123 to silver tapes. Several papers presented the use of additives (Pt, CeO<sub>2</sub>) to affect a size reduction of the 211 second-phase particles during melt processing, with concomitant improvements in  $J_c$  and  $H^*$  properties. Cerium oxide and related cerium-compounds phases were emphasized in this regard. An optimum value for the Ba/Cu ratio was reported which led to improved  $J_c$  and  $H^*$  behavior for melt processed Nd-123 and Sm-123 specimens. A technique was described for producing 211-free Y-123 by use of a Pt-dopant and by carrying out the crystallization at a carefully controlled temperature. The final paper of the session provided new information about phase equilibria in the Bi-Pb-Sr-Ca-Cu-O system near the Bi-2212 and Bi-2223 stability regime. A correlation of Pb solubility in Bi-2212 and Bi-2223 with oxygen pressure and temperature was described and the formation of liquid phases was discussed in the context of their influence on the evolution of the superconducting phases.

In the session of processing of HTS bulk (bulk applications), four talks addressed Y-123 bulk applications. The first talk was on the commercialization of melt-textured Y-123 bulk materials in the



*K. Kajimura (Electrotechnical Laboratory) co-chaired the program committee for the 1997 International Workshop on Superconductivity held at the Royal Waikoloan, Big Island, Hawaii, on June 15–18, 1997.*

form of discs, rods, cylinders, and rings. The reproducibility of obtaining a levitation force of 70 N or less of a 43-mm diameter pellet is 73%. The production cost consists of 50% raw material and 43% labor cost including equipment. Further reductions are to be expected. Possible applications to MAGLEV trains were also presented. Magnetic shielding from a field of 0.1 to 0.01 T is necessary for MAGLEV trains and will be realized by a melt-textured square plate of 90 mm × 90 mm. In a higher field region, shielding is done by the flux-pinning effect. The use of superconducting bulk magnets for the levitation of MAGLEV trains was also investigated by model calculations assuming the array of flux-pinned melt-textured bulk pellets of 100 mm in diameter. To use superconducting bulk magnets, how to magnetize the bulk superconductor is one of the most important engineering problems. The transient behavior of the pulsed magnetization process by using a micro-Hall probe and temperature dependence of the trapped fields were also presented. It was confirmed that the pulsed field magnetization was a simple and effective method as well as the field cooling magnetization. A small motor for a golf-cart and a cryocooler cooled bulk magnet with the pulsed field magnetization using bulk Y-123 materials were introduced. The last talk in the session also focused on cryomagnetic motors. Researchers developed motors up to 1 kW. For a small motor with 400 Hz power supply, a maximum rotation speed of

8,000 rpm was realized.

In the following two sessions of fabrication and control of HTS junctions and applications, recent results on the fabrication of high- $T_c$  Josephson junctions for electronic applications were presented and discussed. Particular attention was focused on the controllability of junction properties, which has significant importance when designing and fabricating integrated circuits such as single flux quantum (SFQ) digital circuits with potential ultrahigh speed performance. Various types of superconductor-normal-superconductor (SNS) and grain boundary junctions with different configurations have been fabricated. Among them, the most well-developed junction with good controllability is the ramp- or edge-type junction with an artificial N layer such as Co-doped Y-123 and Pr-123. As reported in several talks, spreads (1-sigma) in junction critical current  $J_c$  as small as 10% are now obtainable on and off the superconducting ground plane. This value is sufficiently small to operate SFQ circuits containing about 100 junctions. However, the microscopic origin of the spreads is not fully understood yet, though inhomogeneity in effective tunneling area, strong dependence of N layer properties on deposition conditions, and the etching damage and roughness of the edge surface were pointed out as possible origins. Moreover, there is still controversy over the optimum edge angle for smaller spreads. Further investigation is required to achieve much smaller spreads, for instance 5%, necessary to design more complicated SFQ circuits. New results on junctions with "engineered interfaces" were also presented, in which a thin surface layer of the edge was converted to normal by vacuum annealing and plasma treatments. Preliminary results indicated a 1-sigma  $J_c$  spread of 8%. This technique seems promising to reduce the spreads which originate from the variation in N-layer properties as well as surface roughness. As other new approaches to more reproducible junctions, use of a chemically more stable La-doped analogue of 123 compounds as both S and N layers and attempts of fabricating homoepitaxial junctions on large-size Y-123 single-crystal substrates were reported. Because of the expected best crystallinity at the junction interfaces, the latter approach may enable scientists to elucidate the origin of spreads in junction properties as well as to realize more controllable junctions. Results on grain boundary junctions including conventional step-edge junctions, unique junctions fabricated by utilizing a focused-ion-beam technique, and *c*-axis/*a*-axis/*c*-

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axis boundary junctions were also reported. Though some of these junctions were previously used to demonstrate the operation of a quantum flux parametron (QFP) logic gate and an SFQ flip-flop, drastic improvement in the  $J_c$  spreads, typically 35% at present, seems more difficult than the case for edge SNS junctions. Development of low-noise direct-coupled SQUID magnetometers using SNS step-edge junctions with an Ag-Au alloy as the N material was presented. These junctions were shown to have advantages over other types of junctions such as high reliability, which exhibit the 1-sigma  $J_c$  spread almost comparable to that of edge SNS junctions; low levels of the low-frequency noise; and low cost.

In the last session on fabrication and control of HTS junctions and applications, research focused on the SQUID system. Design and fabrication of SQUID devices has remarkably improved and the magnetic field sensitivity of high- $T_c$  SQUIDS has reached close to 10 fT/ $\sqrt{\text{Hz}}$ . The next stage of SQUID system development is finding new fields of application in which detection systems other than SQUID are not applicable or cannot reach the required resolution level. Several application fields were proposed and SQUID systems experimentally demonstrated to be feasible. These were non-destructive evaluation of magnetic impurities, material defects, fatigue, and biomagnetism. Flaws radiating from rivet holes in stacked aluminum plates in aircrafts were detected by mapping the induced current in an ac field, and the layer number of the aluminum plates could be successfully identified by changing the frequency of the external field. For detection of the magnetic particles in wires, iron particles as small as 50 nm in diameter could be detected while wire traveled speed up to 800 m/min. As another example of non-destructive evaluation using the SQUID system, a two-dimensional magnetic flux image was measured for a carbon steel plate with several degrees of plastic deformation. Stripes in the magnetic flux image corresponded to the Luders bands. The ion cluster beam technique was adopted for obtaining a smooth surface of Y-123 films. The smoothness as much as 1 nm was realized by bombardment of ion clusters estimated to be comprised of 2,000 to 3,000 Ar atoms. This smooth surface was realized as a result of both etching at peaks and deposition of the etched particles at valleys.

In the session of thin-film processing for rf applications, LPE Y-123 films on MgO substrates indicated that the misorientation angles between the adjacent grains of the films were less than 1 degree. Therefore the epitaxy films showed high critical current densities both under dc and rf measurements. The deposition method of thermal co-evaporation combined with a moving oxygen pocket heater and a rotating sample holder demonstrated a 20 cm x 20 cm square Y-123 film with  $T_c > 85.5$  K all over the film. The metalorganic chemical vapor deposition (MOCVD) method showed very low surface resistance at 8.5 GHz with smooth and large grain size properties.

In the session of ac losses, vortex dynamics and pinning, seven papers were presented. Although the materials and methods of synthesis presented were very diverse (e.g., Pb-doped Bi-2212 single-crystalline and melt-textured RE-123 and coated Y-123 on metallic substrates) the presentations and discussions focused on methods to enhance the critical current densities  $J_c$  and on the development of an understanding of the underlying mechanisms for vortex pinning in improving  $J_c$ . For example, impressive increases in  $J_c$  were reported in bulk Bi(Pb)-2212, Nd-123, Y-123 (with fission-induced pinning sites) and in coated Y-123 tapes. To identify pinning centers associated with these increases, a number of sophisticated microstructural analysis techniques such as high-resolution

TEM, scanning tunneling microscopy, and high-energy and resolution x-ray diffraction were employed. The pinning sites in question included those which were introduced by controlled precipitation or artificial methods (e.g., fission-induced defects). Some of mechanisms suggested for the pinning sites for the precipitation were very fine scale 2-D modulations of composition in Bi(Pb)-2212, Nd clusters in Nd-123, and the small oxygen deficient regions in YBCO single crystals. Despite detailed microstructural characterization, presentations discussions clearly reflected an incomplete understanding of vortex pinning in these high  $T_c$  superconductors. For instance, the pinning centers in the coated Y-123 thick films and in Nd-123 single crystals are unclear. In addition, while it is known that the irreversibility line in Bi-2212 is significantly improved with lead doping, the direct mechanism, possibly planar compositional modulation or improved electronic coupling along the  $c$ -axis, has not been demonstrated. Thus, this subject is expected to be a topic of extensive discussions in future meetings. Another interesting theoretical presentation concerned the ever

important question of current transport across grain boundaries in Y-123. Here, a model was developed for current transport across the (001) tilt boundary which took into account grain-boundary-area reduction due to edge dislocation cores, which form the boundary, as well as reduced  $T_c$  of the surrounding area via elastic strain associated with the cores. Although the model obviously simplified the structures of the boundary by using only primary dislocations to describe the boundary misorientations and by neglecting the often observed meandering boundaries or secondary dislocations, the predicted pseudo-exponential reduction of the critical current  $J_c$  with misorientation angle agreed well with the experimental self-field  $J_c(0)$  results obtained for the artificially produced bi-crystal grain boundaries in YBCO thin films. In spite of the necessary simplifications of the boundary structures, this appears to represent an important step toward understanding the reduction in  $J_c$  at grain boundaries in high  $T_c$  superconductors.

Nearly a decade has passed since the advent of high-temperature superconductivity. Discovery of new materials and

development of fundamental insight has occurred and continues to occur frequently. In contrast, the progress toward industrialization of the technology has been steadily accelerating. Understanding of crystal growth mechanisms for both thin film and bulk/wire crystals have been deepened, and similarities in thermodynamics, kinetics, and performances of the film and bulk HTS materials especially on processing and crystal growth were well discussed in this workshop, which will help further developments of processes for HTS commercialization. The consensus of the workshop attendees was that most larger-scale applications will require more years to realize, however, and that consistent technological advancement will require worldwide collaborations in at least precompetitive research fields and maintenance of levels of research funding and interest.

### Acknowledgement

I wish to thank all session chairpersons for submission of session summaries for this report.

YUH SHIOHARA  
SRL-ISTEC

## UPCOMING CONFERENCE

### The IV International Seminar-School in Russia to Focus on Phase Transformations and Defect Evolution in Condensed Matter

The IV International Seminar-School will present its conference, "Defect Structures Evolution in Condensed Matter," on September 2-9, 1998 in Barnaul, Russia at Altai State Technical University. This meeting will bring together an international group of scientists to discuss problems connected with crystalline, amorphous, liquid crystalline, and nanocrystalline materials with periodic and aperiodic structures. It will feature papers in the following areas:

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- defects and defect structures and their connection with phase transformation in condensed matter;
- methods of construction of interatomic potentials: *ab initio*, semi-empirical, based on the electron density function;
- structure-energetic aspects of phase transitions in condensed matter;
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- experimental achievements related to problems of transformations in condensed matter;
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- achievements and problems of computer simulation of condensed matter structure-energetic transformations;
- connection of transformations with their physical properties in condensed matter; and
- the problem of integral description of defect and nondefect structures.

Abstract deadline is **November 30, 1997**. The official languages of the symposia are English and Russian. For information on abstract submittal and registration contact Orgcommittee, EDS'98 Headquarters, General Physics Department, Altai State Technical University, 46 Lenin St., Barnaul, Russia 656099; phone 7-385-2-368-522, e-mail: pva@agtu.altai.su. □

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