AN ULTRASONIC SENSOR FOR PROCESS MODELING AND PROCES CONTROL OF CERAMIC SUPERCONDUCTORS

Eva Drescher-Krasicka

Metallurgy Division
National Institute of Standards and Technology
Gaithersburg, MD 20899

The Johns Hopkins University
Baltimore, MD 21218

INTRODUCTION

This research demonstrates the feasibility of utilizing nondestructive ultrasonic sensors to monitor the effects of oxygen content, processing time and temperature on the resultant mechanical, structural, and electrical properties of high temperature ceramic superconductors. Ultrasonic velocity changes, as a function of processing time and temperature, have clearly been shown to indicate the transformation between orthorhombic and tetragonal phases in Y-Ba-Cu-O.

The reversibility of the transition in these 123 compounds provides a good model system for studying the effect of phase changes on ultrasonic velocity. The effects of grain and pore scattering, being essentially constant through the transition, may be eliminated from the result. Newly developed techniques in our laboratories using piezoelectric transducers at high temperatures and improvements in signal recording and analysis provide a method to observe ultrasonic velocity changes which can be related to the changes in microstructure.

It has been experimentally demonstrated that these ultrasonic sensors can continously monitor, up to 1000°C, elastic and anelastic properties of ceramic superconductors. The discovery and development of high temperature ceramic superconductors has provided an opportunity and a need for NDE sensors for this class of materials. These sensors are needed to develop a better understanding of process models and to be used for on-line process control.

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SENSOR

A $LiNbO_3$ ultrasonic transducer was utilized for the ultrasonic velocity measurements. This material has a Curie temperature near 1200°C. However, when in a reduced atmosphere such as vacuum or argon gas, the transducer resistivity decreased on heating above 400°C, such that the ultrasonic signal became undetectable at 600°C. It was found from subsequent high temperature experiments at atmospheric pressure that the "conditio sine qua non" for proper operation of the lithium niobate transducer is a significant partial pressure of oxygen around the crystal. In air, the $LiNbO_3$ works efficiently up to at least 1000°C.

This behavior of the transducer can be explained in terms of the Bollman and Gernand [1] electrical conductivity model for the disorder of $LiNbO_3$.

HIGH TEMPERATURE MEASUREMENTS

Techniques for high temperature ultrasonic measurements in solid materials are not as well developed as ambient and low temperature methods. A critical limitation of high temperature experiments is an acoustic bond between the transducer and the sample. In earlier work [2], we developed a method for overcoming these limitations using a teflon bond under pressure. The extension of this technique to the particular needs of this project utilized a gold foil as a coupling medium between the transducer and the sample. However, it was found experimentally that the best results were obtained with the transducers pressed against the polished, plane parallel sample surfaces without any coupling layer.

The samples were prepared from Y_2O_3, $BaCO_3$ and CuO powders using the solid state techniques described elsewhere [3]. They had a 5% porosity and 20 m maximum grain size. For the ultrasonic measurements, an 8 MHz X-cut (longitudinal) ultrasonic transducer was bonded to the sample using a pressure bond. The sample was pressed against the polished holder base by a system of stainless steel screws. For extended annealing at temperatures near 900°C, an additional system of weights was used in order to keep the pressure constant.

The sample, mounted in the sample holder, was placed in a furnace and the temperature of the sample was monitored by a thermocouple inside the sample holder next to the sample. A separate thermocouple was used as a sensor for the temperature controller. Ultrasonic attenuation and relative velocity changes were measured as a function of time and temperature using a computerized Matec MBS 8000 system.*

The velocity measurements were taken by comparing the phase angle of each echo relative to a continuous sinusoidal reference in phase with the driving pulse. At a given temperature, the velocity change from its initial room temperature value was calculated from a linear least squares fit of the change in phase angle as a function of echo number.

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* The naming of commercial suppliers of instrumentation is given only to identify its specifications and should not be construed as an endorsement by NIST of this product.

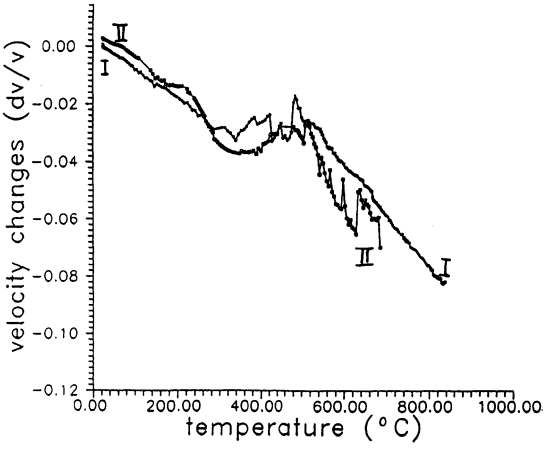

Fig.1 Velocity of ultrasound vs. temperature for heating from orthorhombic to tetragonal phase. Curve I-8MHz, curve II-3MHz data.

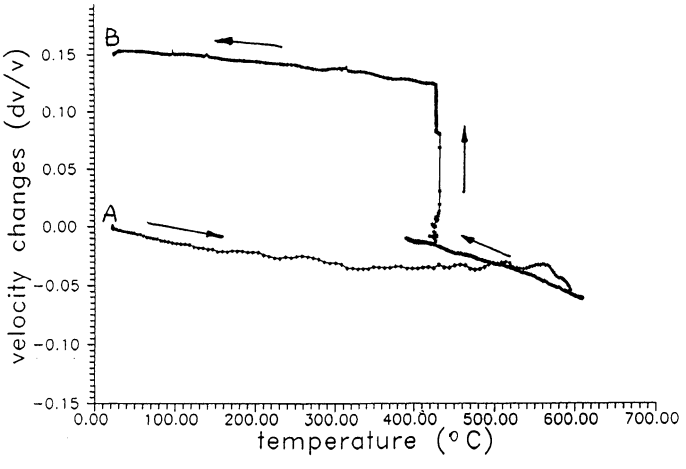

Fig.2 Velocity of ultrasound vs. temperature for processing from tetragonal to orthorhombic phase. Temperature-time dependence for the same experiment is shown in fig.3, the velocity-time dependence is presented on fig.4.

Two different processing cycles on $Y_1Ba_2Cu_3O_{7-x}$ were performed. The first cycle was intended to transform the orthorhombic superconducting phase into the tetragonal phase. This transition occurs around 550°C in air, with the exact temperature being dependent on oxygen content of the sample [3]. The two orthorhombic samples were heated, and the velocity changes as a function of temperature during this warming experiment are shown in fig.1.

Using longitudinal ultrasonic waves, curve I was obtained with 8MHz transducer, curve II with 3MHz transducer. The resultant phase after warming and cooling in the air depends on heating and cooling rate. The 60°K superconducting phase [3] becomes more pronounced with the increasing colling rate (what was not shown in this paper). The correlation between amount of orthorhombic, 90°K phase and observed ultrasonic velocity changes in orthorhombic samples processed in air will be disscused elswhere [4].

The phase transformation from the tetragonal to the orthorhombic structure was also performed in air. A tetragonal sample was prepared by careful annealing in vacuum. The magnetic susceptibility measured after this preparation does not show any superconducting properties. Ultrasonic velocity changes during the annealing of the tetragonal sample are shown in Fig.2. The starting point of the experiment, marked A on the velocity curve, represents the sample in the fully tetragonal state. Ultrasonic velocity changes as a function of processing temperature show the transformation of the tetragonal phase A to the orthorhombic structure B. The arrows indicate sequences of warming, annealing and cooling. The same experiment is shown in fig.3 and 4 as the temperature-time and velocity time dependence. Figure 3 presents temperature changes as a function of processing time. This particular temperature-time sequence was suggested by NIST ceramists for obtaining 90°K T_c from tetragonal, nonsuperconducting pellets. The sample was first heated to 610°C, kept at that temperature and then cooled to 420°C. Starting from the seventh hour of processing, the temperature was held constant for the next 40 hours. During the last three hours of the experiment, the sample was cooled from 428°C to room temperature.

Figure 4 shows the ultrasonic velocity changes as a function of processing time. For the first 4 hours, there are no changes at constant room temperature, the velocity decreases with increasing temperature and increases again on cooling from 600-400°C. The phase transition starts when the sample is kept at a constant 428°C temperature. The velocity of ultrasound continuously increases, first quickly, then more slowly. On cooling, after 40 hours of annealing at constant temperature in air, the velocity increases further. The magnetic susceptibility data as well as the X-ray diffraction pattern show that, at the end of the processing cycle, (marked as point B in Fig. 2-4) the sample has reached an orthorhombic superconducting phase. The ultrasonic velocity is expected to be dominated by changes in lattice parameters associated with oxygen diffusion into the bulk. It is worth emphasizing that the heating and cooling rate for each period of processing is determined by thermocouple measurements. The kinetics of transformation can be evaluated with good accuracy from the data monitored by the ultrasonic sensor and if desired the kinetics of the transformation may be studied as a function of heating and cooling rate, the oxygen partial pressure, or composition.

SUMMARY AND CONCLUSIONS

The high-temperature transition from the tetragonal to the orthorhombic structure in $Y_1Ba_2Cu_3O_{7-x}$ has been monitored in real time

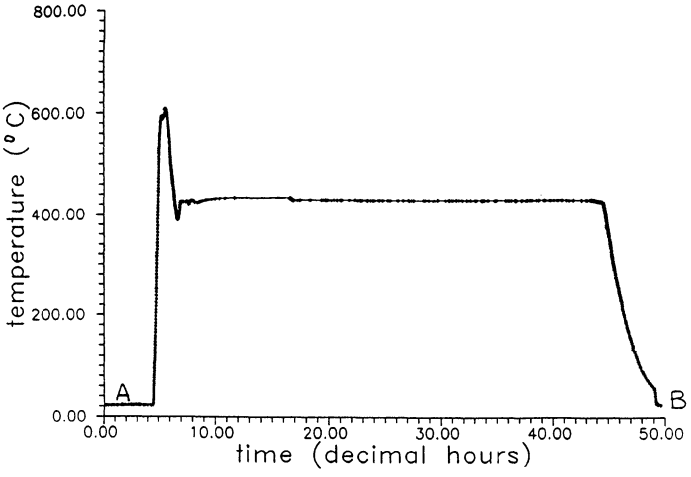

Fig. 3 Annealing schedule for the ultrasonic experiment.

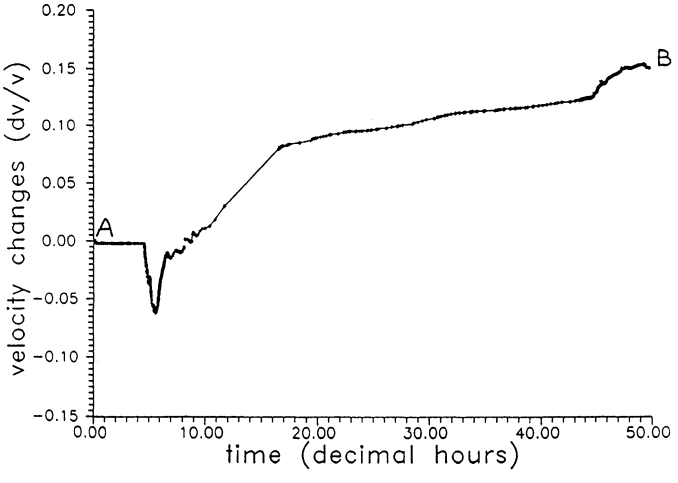

Fig.4 Velocity of ultrasound vs. time of processing. A: the starting point, tetragonal phase. B: finish point, orthorhombic phase.

with an ultrasonic sensor, thus, demonstrating the potential for in-process materials characterization using ultrasonics. The ordered orthorhombic phase is found to have a higher velocity than the disordered tetragonal phase.

ACKNOWLEDGEMENTS

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