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Resistance Measurements in Thick Films of $YBa_2Cu_3O_x$ in the Temperature Range Between 25 and 860°C

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Abstract

The resistance/temperature properties of ceramic thick films of $YBa_2Cu_3O_x$, deposited on alumina substrates, were measured between 25 and 860°C Two identically prepared samples were studied during the course of this work In one case, all resistance/temperature measurements were made in a flowing 21% oxygen atmosphere In the second case, all resistance/temperature measurements were made in a flowing atmosphere of pure oxygen An intriguing minimum in the resistance/temperature curves was observed during the measurements made on both of the samples studied The samples studied also exhibited irreversibility in their resistance/temperature behavior due to thermal cycling

Die Widerstand/Temperatur-Eigenschaften von keramischen $YBa_2Cu_3O_x$-Dickfilmschichten auf Aluminiumoxidsubstraten wurden zwischen 25 und 860°C untersucht Zwei identisch hergestellte Proben wurden fur die Untersuchungen verwendet In einem Fall wurden alle Widerstand/Temperatur-Messungen in fließender 21% Sauerstoff enthaltender Atmosphare gemacht Im zweiten Fall wurden die Messungen in reinem fließendem Sauerstoff vorgenommen Ein unerwartetes Minimum in den Widerstand/Temperatur-Kurven wurde in beiden Fallen beobachtet Die Proben zeigten ein irreversibles Verhalten in ihren Widerstand/Temperatur-Verhalten durch den thermischen Zyklus

Les propriétés de résistance/température ont été mesurées entre 25 et 860°C sur des couches épaisses de céramiques $YBa_2Cu_3O_x$ déposées sur des substrats en alumine Deux échantillons préparés de façon identique ont été étudiés au cours de cette expérience Dans le premier cas, toutes les mesures de résistance/température ont été effectuées sous un courant gazeux contenant 21% d'oxygène Dans le second cas, toutes ces mesures ont été faites sous un courant d'oxygène pur Un très curieux minimum a été observé sur les courbes résistance/température des deux échantillons étudiés Leur comportement résistance/température est irréversible en raison du cycle thermique

1 Introduction

The critical physical properties of the recently discovered ceramic superconductors[1-3] are significantly influenced by the processing and firing conditions used to prepare these materials. In particular, numerous studies concerning the relationships between these conditions and the low temperature (c 90 K) superconducting properties of $YBa_2Cu_3O_x$ ceramic superconductors may be found in the current literature on this subject A representative selection of many of these studies may be found in the five primary sources listed in the reference section of this paper[4-8] Several studies have also involved relatively high temperature resistance measurements on bulk samples of the same ceramic superconductor[9-15] In addition, one study[10] involved high temperature/resistance measurements of sputtered thin films Since high temperatures (typically approaching 1000°C) are almost always employed during the production or processing of these films, a thorough understanding of the real time effects of these conditions upon the film/substrate properties may be very useful In particular, this knowledge could lead to a systematic method of process optimization as well as a technique which might be useful in evaluating

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specific thick film/substrate compatibility With these objectives in mind an experimental research study, directed at measuring the high temperature/resistance behavior of thick films of the $YBa_2Cu_3O_x$ compound, was initiated

2 Experimental Details

Thick film specimens of the $YBa_2Cu_3O_x$ compound were prepared for use during this study using a standard screen printing process [16] These specimens were made with a prefired powdered sample of the $YBa_2Cu_3O_x$ ceramic compound and with other ingredients normally employed to produce thick film screen printable 'inks' The prefired powder was prepared by mixing Y_2O_3, $BaCO_3$, and CuO powders in a Y/Ba/Cu ratio of 1/2/3 so that upon firing, the $YBa_2Cu_3O_x$ compound would form All of this material was initially fired and cooled in a constant flow (1 0 liter/min) of air During the initial firing, the sample was heated from 25 to 470°C in 2 5 h It was held at 470°C for 2 5 h, then heated to 950°C in 2 5 h and held at 950°C for 3 h Then, power to the furnace (a 5 08 cm o d tube furnace) was cut off and the sample was allowed to self cool (within the furnace) back to 25°C

After the initial firing and cooling step, the sample was removed from the furnace, crushed, and ground to a fine powder It was then placed back into the furnace and refired under the same conditions noted above After this second firing, the sample was removed from the furnace, recrushed, and reground into a fine powder The powder was then mixed with other ingredients normally used to produce thick film 'inks' The resulting ink was screen printed upon several prefired 96% alumina substrates The substrate and final film dimensions were approximately 25 mm × 25 mm × 30 μm Two of these samples were fired separately, under identical conditions, in the same tube furnace used to prepare the original powder but a pure flowing oxygen atmosphere (0 5 liters/min) was employed during these firings These firings were required in order to burn out the organic ingredients used to prepare the ink-like coating, and to facilitate both intercrystalline sintering and bonding between the $YBa_2Cu_3O_x$ powder and alumina substrate During this firing step, samples were heated to 950°C in 2 5 h, held at 950°C for 3 h, cooled to 470°C in 2 5 h, held at 470°C for 2 5 h, then furnace cooled Following these firings, two pairs of insulated silver wires were inserted into holes drilled through opposite sides of each sample A small quantity of silver conductive paste (Heraeus Cermalloy—C8710, Heraeus Inc, West Conshohocken, Pennsylvania) was used to bond the silver lead wires to the thick film layer of $YBa_2Cu_3O_x$ Figure 1 contains a detailed drawing showing many of the sample specimen details.

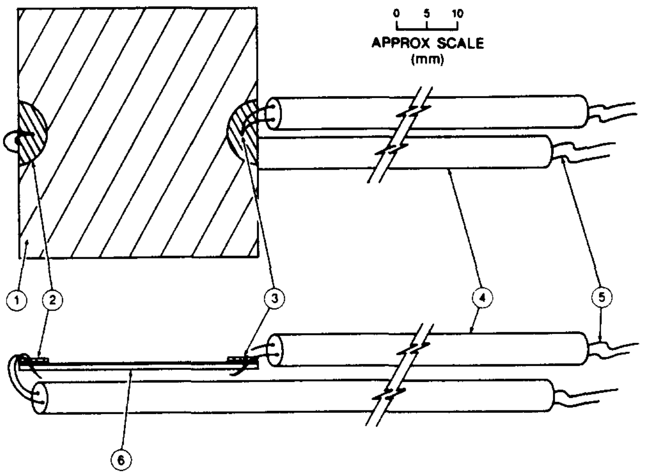

Fig. 1. Schematic diagram showing thick film specimen details 1, Thick film surface, 2, silver paste, 3, holes—0 89 mm i d , 4, ceramic insulators, 5, silver wires, 6, alumina substrate

One of the samples was then placed at the center of the tube furnace Two K-type thermocouples were also positioned under the sample specimen at the center of the tube furnace Electrical leads from a Hewlett-Packard, model 4328A, four wire milliohmmeter (Hewlett-Packard Co, Palo Alto, California) were attached to the free ends of the two pairs of insulated silver wires mechanically attached to the thick film sample at the center of the furnace This sample was fired in a flowing (1 0 liter/min) atmosphere of air It was expected that, after this firing step, the silver paste would form a permanent electrical connection between the silver wires and the thick film sintered powder layer on the surface of the alumina substrate During this firing, the sample was heated to 860°C in 1 h

After this heating process, the furnace and sample were allowed to self cool while the resistance/temperature behavior of the thick film sample was recorded continuously and automatically. A permanent record of the temperature/time cooling behavior of the furnace was also made at the same time

After the initial sample firing (to 860°C) and subsequent cooling, the test specimen was heated two more times but only to 800°C During cooling from 800°C, the resistance/temperature behavior of the sample was measured as indicated above The initial heating to 860°C was chosen to insure complete melting and good bonding between the silver paste, silver wires, and thick film surface layer

Subsequent firings to 800°C were chosen in order to exclude the possibility of remelting the silver paste The recommended paste firing temperature (Heraeus Cermalloy) was between 850 and 920°C

After the experimental work indicated above was completed, the second (and identically prepared) sample was placed in the tube furnace in a flowing (1 0 liter/min) atmosphere of pure oxygen This sample was then taken through the same series of processing and measuring steps as the first sample The main reason for using a second sample for this series of experiments (instead of using the original sample) was related to the fact that each heating/cooling cycle, applied to the original sample, produced irreversible changes in the sample's room temperature resistance

3 Results and Discussion

The primary experimental results obtained during this study may be seen in Figs 2 and 3 Figure 2 is a plot of thick film sample resistance as a function of temperature within a flowing atmosphere of air (21% oxygen) Individual data points are not shown because these curves were recorded continuously as the sample cooled from high temperatures down to ambient temperatures Presumably, one reason for the change in the sample's resistance/temperature behavior, observed during this study, was related to the partial decomposition (or reduction) of the $YBa_2Cu_3O_x$ compound as it was heated Subsequent cooling and reaction with oxygen at lower temperatures[17] tended to restore (nearly) the original resistance of the compound Changes in crystal structure associated with heating/cooling[18-21] and conventional temperature coefficient of resistance (TCR) behavior may have also produced some of the observed changes in the film's resistance There are a number of other interesting features associated with this graph Namely, the resistance/temperature behavior of the thick film sample changed irreversibly after each heating/cooling cycle This phenomenon is probably related to a progressive reaction in the interfacial region between the pure thick film region and the pure substrate region[10,22-32] A scanning electron microscope examination of this interfacial region did indicate a transition zone between the thick film layer and the alumina substrate The SEM study was performed on a separate sample which was fired only once in pure oxygen A photograph of this specimen may be seen in Fig 4 Dual images of the same sample show a back scattered electron image—BSEI (on the left) and a secondary electron image—SEI (on the right) This photograph also allows one to estimate the film layer thickness (approximately 22–38 μm) after a single

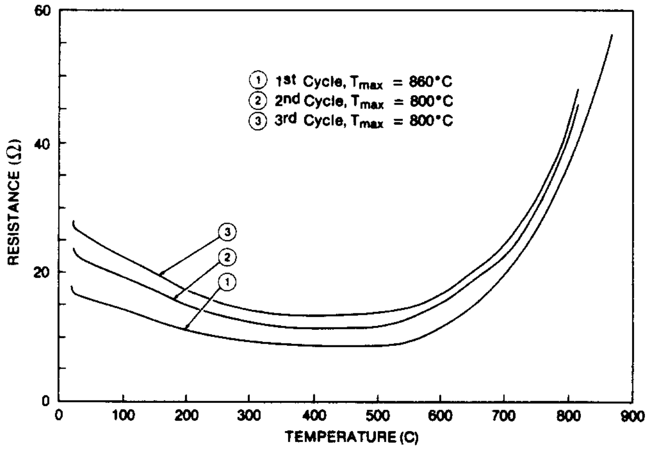

Fig. 2. Thick film sample resistance versus temperature in air

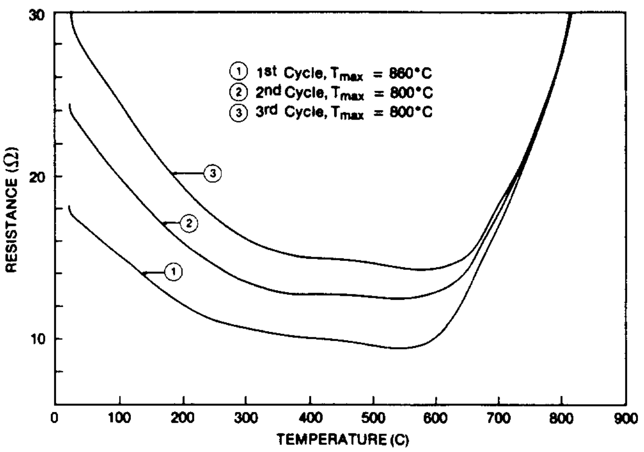

Fig. 3. Thick film sample resistance versus temperature in pure oxygen

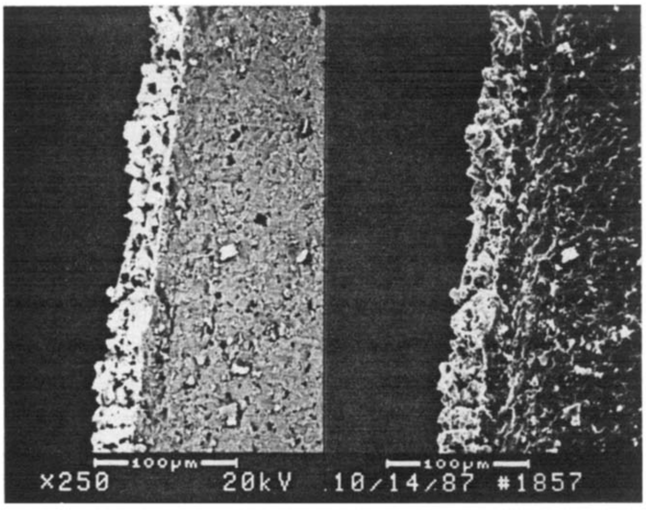

Fig. 4. Cross section of $YBa_2Cu_3O_x$ thick film on alumina substrate

firing in pure oxygen A second possible explanation for the observed irreversible changes in the sample resistance involves progressive destructive fracturing within the thick film layer alone Others have seen evidence of this behavior in individual grains within bulk superconducting specimens which were thermally cycled between 373 and 78 K [33]

Another interesting aspect of the plot in Fig 2 is related to the minimum sample resistance which consistently occurred in the temperature range between 350 and 550°C This observation, of a minimum in the sample's resistivity/temperature curve is the main feature which separates this study from most of the earlier studies, noted above [9-15] In all but one of those studies,[14] no minimum in the resistivity/temperature curves was observed This feature of the data collected may be related to a detrimental interaction between the thick film layer and the Al_2O_3 ceramic substrate If so, the technique employed to collect this data may be a useful (*in situ*, real time) method of evaluating the interaction between other thick film/substrate combinations

Figure 3 is a plot of thick film sample resistance as a function of temperature within a flowing atmosphere of pure oxygen These curves were generated in the same way as the curves presented in Fig 2, except for the use of a pure oxygen atmosphere instead of 21% oxygen The general shape of the curves in Fig 3 are very similar to the curves plotted in Fig 2 However, the minimum resistivity/temperature range is shifted to the right of the corresponding range obtained in 21% oxygen During the first heating/cooling cycle executed using this sample, the minimum sample resistance occurred between 500 and 600°C

Subsequent cycling seemed to shift the minimum sample resistance to higher temperatures This is especially evident if one compares the first and third heating cycle plotted in Fig 3 The thick film resistance values in pure oxygen were also consistently and significantly lower than the sample resistance values measured in 21% oxygen This observation indicates that processing in pure oxygen atmospheres tends to produce samples with lower room temperature resistivities than those processed in less than 100% oxygen In addition, if low room temperature resistivities can be consistently correlated with optimum lower temperature superconducting transition properties, this study provides an interesting guide which may be used to develop more efficient processing methods for producing superconductors from the $YBa_2Cu_3O_x$ compound It may also be pertinent to note here that there is at least one experimental study, involving $YBa_2Cu_3O_x$ films, which has demonstrated significant improvements in zero resistivity temperatures due to 'annealing' these ceramic films in the 550–650°C temperature range in pure oxygen [34] This temperature range correlates very well with the minima seen in the curves in Fig 3

After the high temperature resistance measurements were completed, both of the test specimens were immersed in liquid nitrogen to determine if they would exhibit superconductivity The sample fired in air increased in resistance during immersion in liquid nitrogen but did not become superconducting above 77 K This sample also cracked during the cooling process so it was not possible to obtain an accurate measure of the actual resistance increase at 77 K The sample fired in pure oxygen also exhibited an increase in resistance and did not become superconducting above 77 K Prior to cooling this sample, its room temperature resistance was about 30 Ω At the normal boiling point of liquid nitrogen, the sample's resistance increased to about 66 Ω On subsequent warming, back up to room temperatures (*c* 25°C), the resistance of this sample did not return to its original value The new room temperature resistance stabilized at approximately 49 Ω During the warming process, care was taken to minimize the condensation of atmospheric moisture on this sample in order to prevent any deleterious effects the water could have caused.[35-39]

In another study involving $YBa_2Cu_3O_x$ thick films,[40] a similar resistance increase just above the normal boiling point of liquid nitrogen was observed in some of the samples studied This increase in resistance was followed by a steep drop in resistance which occurred at temperatures below 77 K Two other samples, also examined during that study, became superconducting at 70 and 79 K The authors of that study attributed this behavior to a special processing sequence which involved heating their samples (in flowing oxygen) to 750°C for 4 h, followed by heating to 1000°C for 30 min, then furnace cooling to 25°C Room temperature resistivities reported for these samples were $1 01 \times 10^{-3}$ and $3 0 \times 10^{-3}$ Ω cm In a second study,[34] three thin film specimens of $YBa_2Cu_3O_x$, sputtered on sapphire substrates, became superconducting at 68, 72, and 73 K These samples were annealed in pure oxygen at 600°C and had respective room temperature resistivities of $3 1 \times 10^{-3}$, $1 4 \times 10^{-3}$, and $1 2 \times 10^{-3}$ Ω cm In a third experimental study,[41] thin film specimens of $YBa_2Cu_3O_x$, sputtered on alumina, cubic zirconia, and strontium titanate at 400°C, became superconducting at temperatures as high as 88 K This behavior was attributed to annealing in oxygen for 6 h at 650°C, followed by 1 h at 850°C Room temperature film resistivities ranged between approximately $0\,5 \times 10^{-3}$ and $3 \times 10^{-3}\,\Omega$cm The samples prepared during the present study had initial room temperature resistivities of approximately $5 \times 10^{-3}\,\Omega$cm

In order to test the quality of the ceramic powder used to make the thick films described herein, a bulk specimen was made from the same ceramic powder Approximately 5 0 g of an organic binder (Cerbind—73140, Metoramic Sciences Inc, Carlsbad, California, normally used in ceramic tape casting applications) was mixed with 50 g of the prefired ceramic powder Solvent evaporation at ambient temperatures was allowed to occur over a five day period After this, the solidified block of material was cut into small pieces One of these specimens was fired under conditions identical to those used to initially produce the thick film specimens and attach the silver lead wires This sample was cooled from ambient temperatures down to the normal boiling point of liquid nitrogen, then allowed to warm very slowly During this period, four wire resistance measurements indicated zero resistivity below 80 K, a steep increase in resistivity between 80 and 91 K (reaching approximately $2\,3 \times 10^{-3}\,\Omega$cm at 91 K) and a practically linear increase in resistivity between 91 and 300 K (reaching approximately $4\,9 \times 10^{-3}\,\Omega$cm at 300 K) This final room temperature resistivity compares very well with the original room temperature resistivities of the thick film samples prepared during this study

4 Conclusion

This experimental study has demonstrated that $YBa_2Cu_3O_x$ thick films (on alumina substrates) exhibited a minimum resistance in the temperature range between 350 and 650°C In addition, the samples studied also exhibited irreversibility in their resistance/temperature behavior due to thermal cycling These effects were observed in processing atmospheres consisting of either 21% or 100% oxygen The exact reason for, and significance of, this behavior is still not well understood However, at present, it is believed that these effects are due primarily to a progressive chemical interaction between the $YBa_2Cu_3O_x$ thick film layer and the alumina substrate This effect also has a detrimental influence upon the superconducting–zero resistivity transition temperature of thick films of $YBa_2Cu_3O_x$ fired on alumina substrates The technique disclosed herein can also be applied to many other electrically conductive ceramic thick (or thin) film/substrate combinations This may permit one to quickly, and in real time, measure the relative interaction between these film/substrate pairs Subsequent correlation between the specific film/substrate pairs, processing conditions, and *in situ* resistance/temperature behavior may also reduce the need to rely upon the trial and error approach in evaluating superconducting ceramic atmosphere processing conditions Experimental studies, such as these, are presently underway in our laboratories and will be reported on at a later date

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