WET CHEMICAL PROCESSING OF HIGH T_c SUPERCONDUCTING FILMS

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ABSTRACT

The present investigation relates to the processing of high temperature superconducting films by employing simple techniques such as spraying solutions of desired cation species, as yttrium, barium and copper, onto ceramic substrates. The films are free of cracks and possess good mechanical properties such as resistance to scratching. Superconducting transition temperatures (T_c) as high as 94°K have been observed in these films as determined by four-probe electrical resistivity measurements.

INTRODUCTION

The announcement of superconductivity above 30°K in the La-Ba-Cu-O system (1) and the discovery of superconductivity in the Y-Ba-Cu-O system (2) have spurred great interest in utilizing these materials technologically. Soon after Wu, et al. (2) announced their discovery of the Y-Ba-Cu-O system, important properties of the Y-Ba-Cu ceramic came to be known. Rao, et al. (3) demonstrated by X-ray diffraction studies that the superconductor discovered by Wu et al. was actually polyphasic and that the black phase with the composition $YBaCu_3O_{7-\delta}$ (where δ = 0.1-0.2) was responsible for superconductivity. Rao also demonstrated that another phase, which is green in color, has the stoichiometry Y_2BaCuO_5 and is non-superconducting. Subsequently, other groups (4) confirmed the X-ray work of Rao and determined the crystal structure of the black phase.

Several other important facts regarding the Y, Ba, Cu 1,2,3 phase have since come to be known. Beyers, et al. (5) determined that at temperatures of 500-600 C, the 1,2,3 phase undergoes a tetragonal-to-orthorhombic transformation; and the latter is the superconducting phase. The oxygen sotoichiometry of the 1,2,3 compound has been found (6) to affect the transition temperature and the sharpness of the transition from the normal to the superconducting state.

After the Y-, Ba- and Cu-compounds are formed into bulk shapes or films, the samples are fired at about 950 C for sintering and elimination of $BaCo_3$. During the firing stage, the 1,2,3 phase becomes tetragonal; and a considerable amount of oxygen is lost. The stoichiometry of the 1,2,3

compound at 950°C becomes $YBa_2Cu_3O_{6.5}$ (6). To ensure that the tetrogonal-to-orthorhombic transition is brought to completion, cooling in the temperature range (500-700)°C should be performed slowly. Beyers, et al., have established that annealing the 1,2,3 material at (500-600)°C in flowing oxygen for a prolonged period results in the proper stoichiometry of oxygen to cations which makes the material superconducting.

The discovery of superconductivity at temperatures above that of liquid nitrogen has opened up new vistas of possible industrial application. Processing of thin films has many potential technological applications for these superconducting materials. References 7-9 outline the state of the art in this field. The techniques for depositing superconducting films on various substrates comprise electron beam evaporation, molecular beam epitaxy, sputtering and pulsed laser evaporation. These techniques invariably require high vacuum (as 10^{-6}-10^{-7} Torr) and expensive equipment. The superconductive transitions that have been reported in these studies are in the range 60°-95°K depending on the type of substrate and the firing and annealing procedures employed.

The high vacuum conditions required for the existing techniques for depositing superconducting films require skilled operators. The evaporation or sputtering targets have to be prepared in the form of alloys which are expensive to prepare. Moreover, it is economically unattractive to coat large objects with these techniques. These problems can be overcome by wet chemical processing which involve inexpensive machinery and relatively unskilled operators.

There has been one unsuccessful attempt to process superconducting films on ceramic substrates by spraying solutions of yttrium, barium and copper compounds (8). Henry, et al. (8) outline this effort and state that attempts to measure the resistivity of the annealed films were unsuccessful because the films were extensively cracked. In other words, superconductivity was not observed; and a continuous film, covering the surface of the substrate, was not achieved.

Chiang, et al. (10), have prepared bulk and thin films of superconducting materials from liquid citrate precursors. Thin films were coated on substrates by spin-coating or dip-coating. Heating the film produced superconducting oxides on the substrate.

The present investigation describes the processing of films by spraying or otherwise depositing nitrate solutions of cation combinations such as Y, Ba and Cu on ceramic substrates. After firing, the resulting oxide films exhibit superconductivity up to temperatures similar to those of films obtained by vacuum deposition techniques.

Experimental Procedure

A. Preparation of Solutions

The cations, preferably in the stoichiometric ratio (e.g., for the Y-Ba-Cu system, the ratio is 1,2,3) are incorporated in a clear solution. The solution can be aqueous, whether acidic, neutral or basic. Compounds, such as the oxides, nitrates, carbonates or hydroxides or a combination of these,

can be dissolved in acids or water. Mild heating associated with stirring may be necessary to obtain a clear solution. It is beneficial to have a saturated solution; but care must be taken to ensure that no precipitate is formed.

B. Substrate Preparation

The substrate can be a metal, a ceramic or a glass. The substrates should be cleaned adequately so that the surface is free of dirt or any organic material which may interfere with the adherence of the film to the substrate. The substrates should preferably be heated to a suitable temperature which is high enough that a drop of solution will evaporate relatively rapidly on contact. Once this temperature has been established, the surface of the substrate should be maintained at that temperature while the film deposition is carried out. It has been observed that there exists an optimum temperature range for a substrate-solution combination which facilitates formation of a good film. For the 1,2,3 system, this temperature range is 170-190°C when partially stabilized zirconia is used as substrate. An unduly low substrate temperature results in a wet film; and the desired stoichiometry is difficult to maintain. The less soluble components tend to precipitate, whereas the more soluble components tend to remain in solution and tend to get washed away during successive depositions. Moreover, problems of local non-stoichiometry arise if an unduly low substrate temperature is used. An unduly high substrate temperature has also been found to result in defective films which are patchy in texture and may contain numerous cracks.

C. Film Deposition

The following film-deposition methods have been employed:

Technique I: The deposition of the film may be carried out by depositing the solution onto hot substrates in the form of small drops, one drop at a time. The substrate is kept flat on a heat source such as a hot plate; and drops of the solution are added at regular intervals to the substrate. The liquid spreads over the substrate on contact and dries rapidly, leaving a film on the substrate. After a drop is added to a substrate, the surface temperature may drop by as much as 20°C or more. Sufficient time must be allowed before adding the next drop for the temperature to rise back to the desired level. The number of drops required to form a film depends on the surface area of the substrate, the solute concentration of the solution and the size of the drop.

Technique II: Solutions prepared as described earlier may be sprayed with a spray gun onto suitable substrates, the surfaces of which are heated and maintained at a pre-determined temperature. The substrate is kept flat on a hot plate; and spraying is preferably done from a position located vertically on top of the substrate. Spraying the solution from a single side (i.e., lateral spraying) typically results in a film that is deficient in the more soluble species in the solution. The reason for this deficiency is likely that the more soluble components are washed away during successive spraying cycles. When spraying is carried out from the top of the substrate, the washing away of the more soluble components can be avoided. To prevent further loss of the more soluble components, spraying should be performed

intermittently, making sure the already deposited film is at the pre-determined high temperature. After each time the solution is sprayed, the temperature of the film decreases. Enough time should be allowed between spraying to permit the top of the substrate to return to the desired temperature. The number of spraying cycles which is required depends on parameters such as the type of spray gun, the area of the substrate being coated, the concentration of the solution and the film thickness required.

D. Firing and Annealing Procedures

The films deposited by any of the techniques described above are ready to be fired immediately thereafter. The firing may conveniently be carried out in horizontal tube furnaces; but other furnace geometries may be used as well. The furnaces should have attachments for flowing oxygen gas during the heat treatment. Each superconducting system has its own firing and annealing schedules. These depend on the chemical composition of the oxides as well as the physical and chemical nature of the respective superconducting phases. The following firing schedule was found to be useful for obtaining good performance of Y-Ba-Cu films:

i) The sample is introduced into the furnace at room temperature; and the firing through step viii below is carried out in a laboratory atmosphere;

ii) The furnace temperature is raised to 150°C at the rate of 10°C per minute and held at 150°C for 1 hour. This step removes moisture adsorbed from the atmosphere;

iii) The furnace temperature is raised to 300°C at the rate of 10°C per minute and held at 300°C for 1 hr.

Depending on the starting materials from which the solution is prepared, a long soaking period may be desired at temperatures where the volatile species (decomposition gases) start evolving. For Y-Ba-Cu-O films prepared from the respective nitrates, the decomposition of the nitrates takes place in the temperature range 400°-600°C. To facilitate removal of the decomposition gases, the rate of heating in this temperature range should be low. The following heating schedule is useful for Y-Ba-Cu-O superconducting films prepared from nitrate solutions, but other schedules may also be employed with success. It is not suggested to represent an optimal firing schedule.

iv) The furnace temperature is raised to 400°C at the rate of 5°C/minute and held at 400°C for 3 hours;

v) The furnace temperature is raised to 550°C at the rate of 5°C/minute and held for 4 hours;

vi) The furnace temperature is raised to 620°C at the rate of 5°C/minute and held at 620°C for 6 hours.

vii) The furnace temperature is raised to 880°C at the rate of 5°C/minute and held at that temperature for 12 hours;

viii) The temperature is increased to 925°C at the rate of 5°C/minute and held at that temperature for 6 hours;

ix) The flow of oxygen through the furnace is started after the sample has been heat-treated in air at 925°C for 3 hours. The oxygen gas flows from a pressurized gas cylinder through the tube such as quartz or mullite which contains the sample in the furnace. The gas flows in through one end of the tube and is collected at the other end to be led into a test tube containing mineral oil (bubbler). The flow of oxygen gas can easily be controlled by adjusting the value of the gas regulator attached to the gas cylinder. The rate of oxygen flow is maintained at 2-3 bubbles per second in the gas bubbler;

x) After soaking the sample in oxygen at 925°C for a total of six hours, the sample is furnace-cooled at the rate of ~2°C/minute to 550°C while the oxygen flow is maintained. At 550°C, the sample is oxidized for 16 hours to attain proper oxygen stoichiometry and to allow the tetragonal to orthorhombic transition to take place;

xi) After the oxygen treatment, the sample is cooled to ~80°C in about 6 hours while the oxygen is kept flowing; and

xii) The sample is removed from the furnace at ~80°C and promptly dessicated.

The rationale behind the slow heating rates cited above is to allow the film and the substrate to adjust to the thermal expansion mismatch. The long soaking period from 400°C to 620°C seems important (although it might well be shortened) because in this temperature range the gases resulting from the decomposition of the nitrates evolve. Sintering of the film starts at temperatures in the range of 650°C. If all the gaseous products of nitrate decomposition are not allowed to diffuse away from the film, the porosity of the film may increase, resulting in increased resistivities of the samples. A prolonged soaking at 880°C facilitates improved sintering of the film, giving it a good connective texture. The films are black in color and no cracks or apparent defects are observed.

RESULTS

A. Superconducting films in the Y-Ba-Cu-O system were processed by starting with the nitrates of Y, Ba and Cu. A 10 gm batch of the nitrates was prepared with the Y:Ba:Cu ratio of 1:2:3. The weighed batch was dissolved in ~100 ml distilled water. Mild heating gave a clear blue solution in about 10 minutes.

The solutions were sprayed with a spray gun onto partially stabilized zirconia substrates, the surfaces of which were heated to ~170°C. The substrates were kept flat on a hot plate; and spraying was done from a point located vertically on top of the substrate. Spraying the nitrate solution from a single side (i.e., lateral spraying) can result in a Ba- and Cu-deficient film. The reason for this deficiency when observed is likely that the Ba and Cu nitrates have greater solubilities in water than yttrium nitrate. During spraying from one side, the more soluble Ba and Cu ions can be washed

away from the film. This renders the film a green color after the firing and oxygen-annealing treatments.

The green phase likely had the composition, Y_2BaCuO_x; and films prepared by lateral spraying often have a green majority phase. When the nitrate solution was sprayed from the top of the substrate, the Ba and Cu did not wash away as easily; and the green phase was typically completely absent in these films. After each time the solution was sprayed, the temperature of the film typically decreased to ~155°C. Enough time was allowed between spraying to allow the top of the substrate to get back to temperatures in the range of 170°C. The number of spraying cycles required depended on the type of spray gun, the area of the substrate and the concentration of the solution. Black films devoid of any crack or apparent defect were obtained.

The samples were ready to be fired immediately thereafter. The firing and annealing schedules applied to these samples were those presented above (Steps i-xii).

Standard four-probe electrical measurements were performed on the films. Silver electrodes were pasted on the film with silver paint. The resistance vs. temperature plot is provided in Figure 1. The critical temperature is observed to be 94°K. Other similarly prepared samples exhibited critical temperatures ranging from 85°K to 94°K. The reproducibility of the resistance values in different samples having the same film thickness is estimated at ~5%. The error involved in temperature measurement was ±1°C.

X-ray diffraction experiments using Cu Kα radiation were performed on the film. The plot of intensity vs. scattering angle 2θ has close resemblance to the X-ray diffraction pattern of Rao, et al. (3), for the $YBaCu_3O_7$ phase.

B. Superconducting $YBa_2Cu_3O_{7-\delta}$ films on suitable ceramic substrates were deposited by adding drops of the nitrate solutions of Y, Ba and Cu onto heated substrates. An aqueous solution of the aforesaid cations in the proper stoichiometry (Y:Ba:Cu:1:2:3) were made from their nitrates as described before.

The film was deposited on a partially stabilized zirconia substrate by adding droplets of the nitrate solution (one drop at a time) onto the heated substrate. The substrate was kept flat on a hot plate, the top surface of which was maintained at a temperature of about 170°C. The solution drop spread on contact with the substrate and immediately formed a black dried film. Repeating this step a number of times resulted in a black film covering the substrate completely. The number of drops required to obtain a suitable film was found to depend on the concentration of the solution, the area of the substrate and the volume of each drop. Such film deposition has been performed on partially stabilized zirconia substrates. A wide range of other substrates, including strontium titanate, aluminum nitride, barium titanate, alumina and magnesia, can also be employed to good advantage.

The firing and annealing procedure was the same as described above. A continuous, defect-free film was formed, which had the electrical characteristics shown in Figure 2.

Films of Varying Thicknesses

A series of 1,2,3 films having varying thicknesses were deposited by spraying nitrate solutions of the Y, Ba and Cu compounds on partially stabilized zirconia substrates. The normalized resistance vs. temperatures plots of these films are shown in Figs. 1,3 and 4. For a film having a thickness of approximately 15 μm, a superconducting transition temperature of 94°K is achieved. As the thickness of the film is reduced to 7-8 μm, zero resistance above liquid nitrogen temperature is not observed. However, a sharp transition onset occurs at around 90°K. Similarly, with a film thickness of 3-5 μm, a transition is observed at around 90°K and zero resistance is not observed above liquid nitrogen temperature. It is interesting to note that the T_c onset is 90°K for both the 3-5 μm and 7-8 μm films. However, a larger drop in resistance is observed in the 7-8 μm film. These results point to the poisoning effect of the substrate. With a thick enough film (~15 μm), the top few layers are expected to be relatively free from substrate interaction and hence superconducting transition temperatures of around 94°K is achieved. The superior electrical characteristic of the 7-8 μm film over the 3-5 μm film indicates that the extent of substrate interaction was greater in the case of the thinner film.

Makous, et al. (11), have demonstrated the effect of the contamination interaction of superconducting films with substrates. Substrate interaction lowers the critical temperature; and the transition from normal to superconductive state is also lost to a certain extent. It was shown that a thin layer of relatively unreactive material, such as ZrO_2 or metallic silver, between the substrate and the superconducting film considerably reduces the poisoning effect of the substrate. It is, therefore, expected that using a suitable buffer layer between the substrate and a wet chemically deposited film may reduce the poisoning effect. This may result in thinner films with good superconducting characteristics.

CONCLUSION

High T_c superconducting films can be deposited on various ceramic substrates employing simple wet chemical processing techniques. These films have been found to adhere well to the substrates. They exhibit high T_c values which are comparable to those of films prepared by vacuum deposition techniques.

ACKNOWLEDGMENTS

Financial support for the present work was provided by the Air Force Office of Scientific Research. This support is gratefully acknowledged.

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FIG. 1

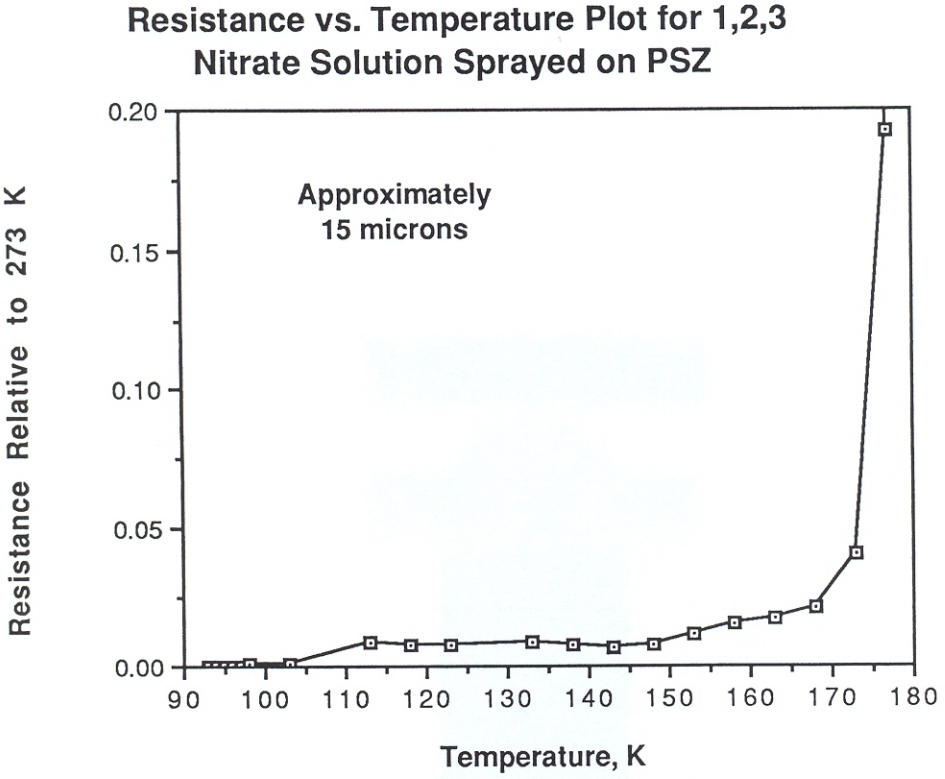

Resistance vs. Temperature Plot for 1,2,3 Nitrate Solution Sprayed on PSZ
Approximately 15 microns
Resistance Relative to 273 K
0.20
0.15
0.10
0.05
0.00
90
100
110
120
130
140
150
160
170
180
Temperature, K

FIG. 2

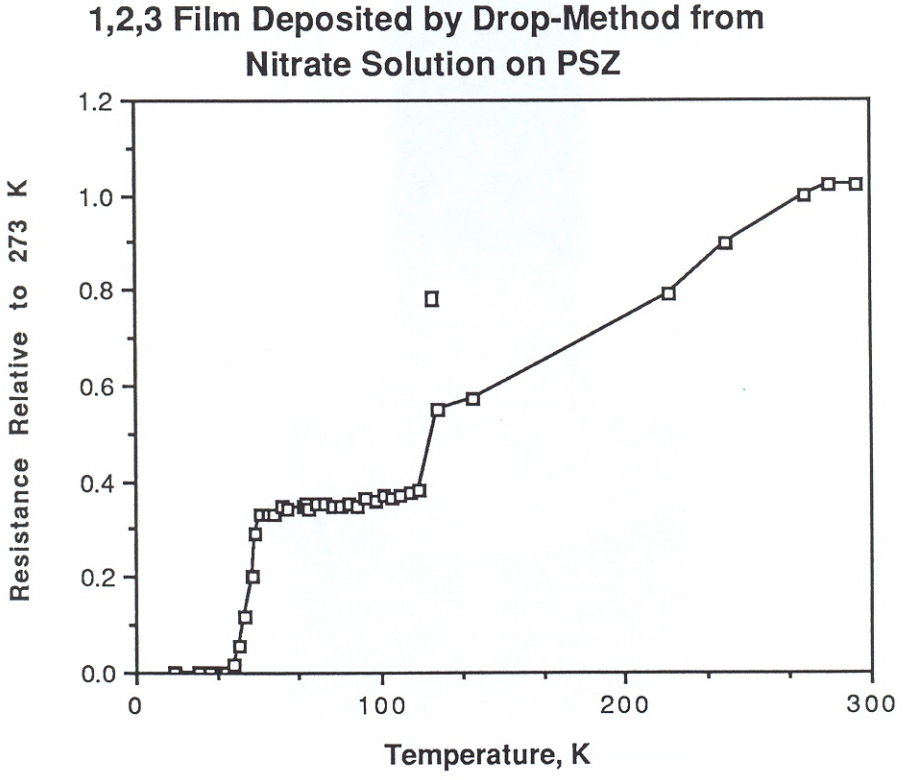

1,2,3 Film Deposited by Drop-Method from Nitrate Solution on PSZ
Resistance Relative to 273 K
1.2
1.0
0.8
0.6
0.4
0.2
0.0
0
100
200
300
Temperature, K

FIG. 3

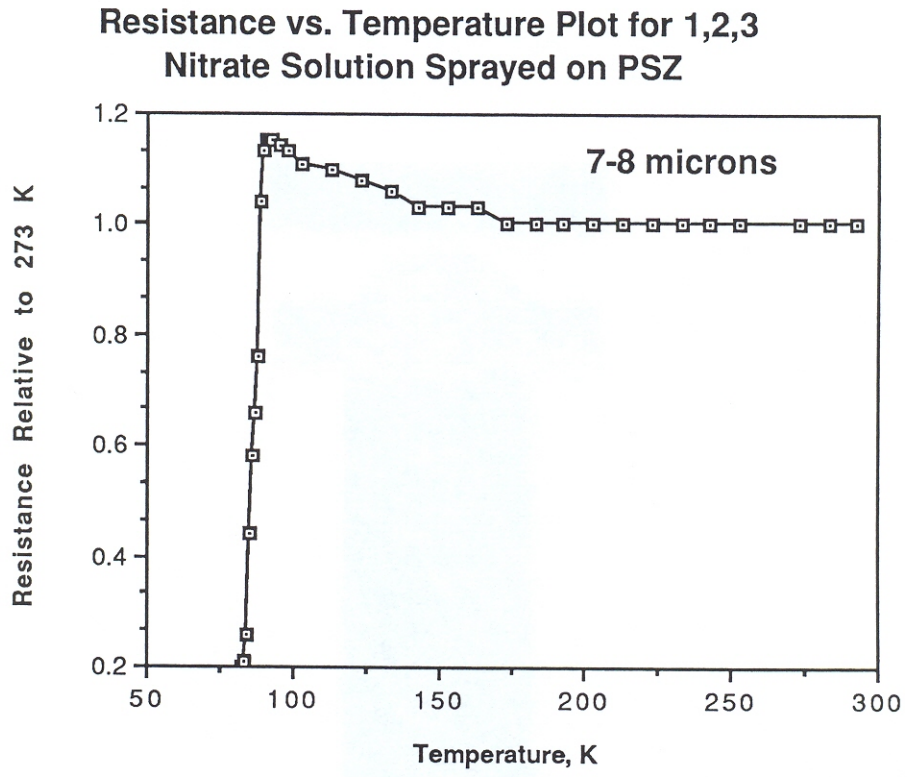
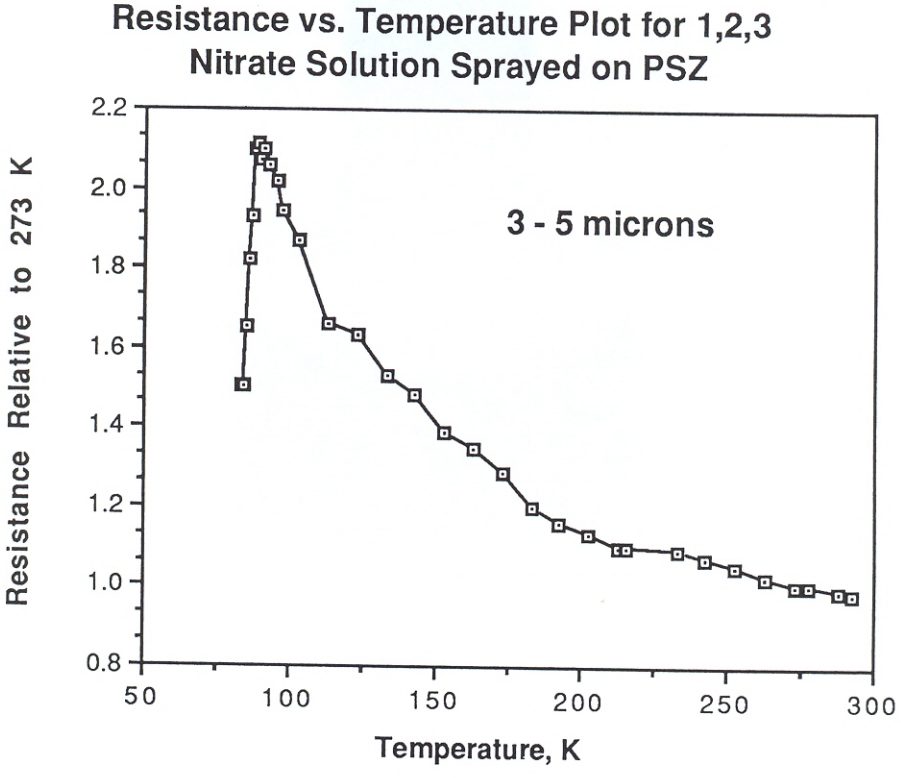

Resistance vs. Temperature Plot for 1,2,3
Nitrate Solution Sprayed on PSZ
7-8 microns
Resistance Relative to 273 K
Temperature, K
1.2
1.0
0.8
0.6
0.4
0.2
50
100
150
200
250
300

FIG. 4


Resistance vs. Temperature Plot for 1,2,3
Nitrate Solution Sprayed on PSZ
3 - 5 microns
Resistance Relative to 273 K
Temperature, K
2.2
2.0
1.8
1.6
1.4
1.2
1.0
0.8
50
100
150
200
250
300