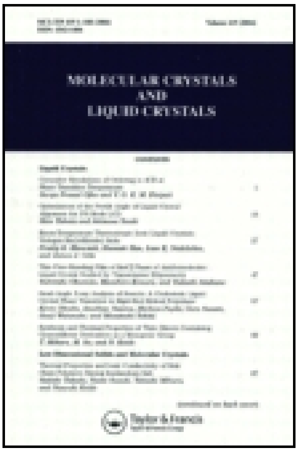

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Sumio Sakka [a], Hiromitsu Kozuka [a] & Haoren Zhuang [a]
[a] Institute for Chemical Research, Kyoto University, Uji, Kyoto-Fu, 611, Japan
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SUPERCONDUCTING OXIDES PREPARED BY SOL-GEL PROCESS

SUMIO SAKKA, HIROMITSU KOZUKA and HAOREN ZHUANG
Institute for Chemical Research, Kyoto University,
Uji, Kyoto-Fu 611, Japan

Abstract High Tc superconducting oxides are ceramics and brittle, which makes it difficult to form long wires for magnet coils and electric power transmission. In this paper, the application of sol-gel process to preparation of superconducting coating films and fibers, which might lead to long wires in future has been reviewed. It has been shown that superconducting coating films and fibers of the Y-Ba-Cu-O and Bi-Sr-Ca-Cu-O systems can be obtained but so far the superconducting properties of both coating films and fibers are not sufficient for the practical application as wires and, for fibers, the mechanical property is poor. It can be stated, however, the improvements of the properties may be possible.

INTRODUCTION

High Tc ceramic superconducting materials can be applied to high electric current wires for coils of magnets producing strong fields and power transmission besides the application to electronics. The extensive efforts so far made for applying the superconducting metallic alloy of the Nb-Ti system with Tc at 9.8 K to practical use have indicated that the most suitable construction of the high current wires is a copper matrix embedded with many thin superconducting metal fibers.[1] In order to apply this idea to high Tc superconductors, long thin fibers or tapes have to be prepared for constructing wires. It should be remembered that the fiber formation from oxide powders is not easy compared with metallic alloys. There are three classes of the method of preparing wires as shown in Table 1. Preparation of superconducting coating films and fibers by the sol-gel method will be reviewed on two types of high Tc superconducting ceramics of the Y-Ba-Cu-O[2] and Bi-Sr-Ca-Cu-O[3] systems.

COATING WITH THE SUPERCONDUCTING OXIDES BY THE SOL-GEL METHOD

Coating of metallic or ceramic fibers or long tapes with superconducting oxide would serve in producing superconducting wires. Most of the results of studies on coating carried out so far with plate-shaped substrates would be easily applied to long wires with a round cross-section or long tapes.

It is known that well-controlled vapor deposition techniques give superconducting oxide coating films with high Tc and Jc.[4] For practical production, however, the coating using solutions will be advantageous due to its higher productivity. Since the film is assumed to take the gel state in the solution coating, the word sol-gel process will be utilized for all the solution techniques in this article.

TABLE 1 Methods for producing continuous wires and fibers of high Tc superconducting oxides.

(1) Superconducting oxide powder processing:
- Mechanical elongation of powder packed in a metal tube.
- Elongation of cylindrical powder compacts with plasticizing agent.

(2) Coating on ribbon-shaped substrate:
- Vapor phase deposition.
- Sol-gel coating.

(3) Liquid phase drawing:
- Fiber formation from the melt.
- Fiber drawing from the viscous solution.

Significance of the Sol-Gel Method as Applied to Superconducting Oxides

Generally, in the sol-gel method,[5,6] compounds of metals corresponding to target oxides, such as metal alkoxides, other metal-organic compounds and soluble inorganic compounds are dissolved in solvents, such as alcohol and water, the solution is gelled by chemical reaction of the compounds and the gel is converted to a ceramic or glass. The most important advantage of the sol-gel method is the possibility for the low temperature preparation of dense, well-sintered ceramics. It should be also noted that the sol-gel method facilitates preparation of coating films and fibers.

Although the advantage of the possible low temperature sintering and resulting occurrence of homogeneous product are not displayed to a high degree in preparation of high Tc ceramics so far, there are some examples indicative of advantages of the sol-gel method.

Comparison of the x-ray diffraction pattern of Y-Ba-Cu-O material derived from gels consisting of metal acetates heated at a rate of 5 °C/min to 750 °C and kept there for 19 h with that of the product made by heating the pellet of a mixture of conventional raw materials carbonate and oxide powders indicated[6] that the sol-gel method gives $YBa_2Cu_3O_{7-\delta}$ crystalline phase at 750 °C, while the conventional powder mixture does not. Shibata et al.[7] made superconducting $YBa_2Cu_3O_{7-\delta}$ ceramics from a pellet consisting of fine particles precipitated from the butanol solution of metal alkoxides, indicating that the sintering takes place at lower temperatures compared with a conventional powder mixture. Hirano et al.[8] obtained a single phase $YBa_2Cu_3O_{7-\delta}$ crystalline phase at 750 °C, while the solid state reaction did not give $YBa_2Cu_3O_{7-\delta}$ phase at that temperature. The decrease in formation and sintering temperatures can be attributed to homogeneous and fine nature of particles in the sol-gel processing.

Sol-Gel Derived Superconducting Coating Films

The sol-gel coating starts with preparation of a homogeneous solution of the compounds containing pertinent metallic elements. Metal-organic compounds, metal alkoxides and inorganic salts are employed as starting compounds.[7,9-18] The solution is then applied to the substrate by dip-coat, spin coat or dripping near room temperature. After gelation and drying, the film with the substrate is heated to high temperatures in the range of 700 - 950 °C, where the superconducting crystalline phase appears in the Y-Ba-Cu-O and Bi-Sr-Ca-Cu-O systems. It is important to utilize less reactive materials as substrate, so that the deterioration of the superconducting properties resulting from the reaction of the film with the substrate might be minimized. Yttria-stabilized zirconia (YSZ) and single crystal magnesia (MgO) are suitable as substrate. In order to obtain wires, the fibers with round cross-section or long ribbons (tapes) are needed for the substrate. It will be possible that sol-gel derived stabilized zirconia fibers[19] might serve as such fibrous substrate.

It is noticed that some of the coating films on a single crystal substrate have orientation of superconducting crystals. Since superconducting oxide crystals are anisotropic in crystalline structure and so in superconductivity,[20] creation of favorable crystal orientation would produce an excellent superconducting wire.

An Example for Preparing $YBa_2Cu_3O_{7-\delta}$ Coating Films

Our experience in preparing $YBa_2Cu_3O_{7-\delta}$ coating film[6,14] is described in more detail. Metal alkoxides $Y(n\text{-}OC_4H_9)_3$, $Ba(OCH_3)_2$ and $Cu(OCH_3)_2$ have been employed as starting compounds. $Ba(OCH_3)_2$ was synthesized by putting small pieces of Ba metal into methanol. $Y(n\text{-}OC_4H_9)_3$ in xylene was dissolved in methanol-triethanolamine solution. The addition of triethanolamine is made to dissolve the copper alkoxides, which cannot be dissolved in alcohol-water solutions. To methanol-triethanolamine solution of $Y(n\text{-}OC_4H_9)_3$, $Ba(OCH_3)_2$ and $Cu(OCH_3)_2$ were added to make a homogeneous, dark-blue starting solution. The solution was dripped on the YSZ plate substrate. After drying, the film with the substrate was heated at 800 °C for 5 min. The application process consisting of dripping of the solution, drying and heating at 800 °C was repeated for 5 - 10 times, so as to have the final film thickness larger than about 5 μm. Then the film was heated in an oxygen atmosphere at 800 °C for 50 - 80 h and cooled in the furnace.

A scanning electron microscopic picture of the cross-section of the film indicates that the film consists of grains about 1 μm in diameter. As shown in Fig. 1, film of 7 μm in thickness has Tc(onset) at 95 K and Tc(end) at 56 K. Further efforts should be made to raise Tc(end) by optimizing the heat treatment.

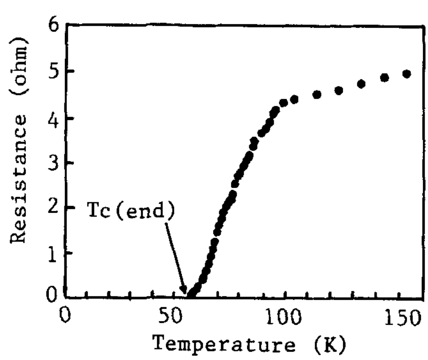

FIGURE 1 Electrical resistance of a $YBa_2Cu_3O_{7-\delta}$ coating film prepared by the sol-gel method using metal alkoxides.[14]

SOL-GEL SYNTHESIS OF SUPERCONDUCTING FIBERS

As shown in Table 1, the liquid phase fiber formation includes the fiber formation from a melt and the fiber drawing from a viscous sol. For the $YBa_2Cu_3O_{7-\delta}$ superconductor, the fiber formation from a melt consists in the solidification of the high temperature melt poured and quenched in a fiber-shaped mold. Since the viscosity of the melt is too low for fiber drawing and the solidified product is hard and brittle, this method is not suitable for preparation of long, continuous wires.

Some melts of the compositions corresponding to the Bi-Sr-Ca-Cu-O superconducting oxide phases can be quenched into glass.[21] This might let one presume that fibers could be made by drawing from the melt through orifices as is done in the silicate glass fibers or elongating a heated rod. A group of Sumitomo Electric Industries Company[22] succeeded in drawing glass fibers from a Bi-Sr-Ca-Cu-O rectangular glass rod to convert to superconducting fibers.

Here, the fiber formation based on the sol-gel method is described. The sol-gel preparation of superconducting oxide fibers consists in fiber drawing from a viscous solution near room temperature and heat treatment of the resultant gel fibers to precipitate superconducting crystals.[23-30] In order to draw fibers, a viscous solution or slurry is prepared by adding viscosity-increasing agents such as polyvinylalcohol and methacrylic acid to a solution of pertinent metal compounds or a slurry containing a fine superconducting oxide powder. A viscous solution can also be made by reacting a homogeneous solution containing pertinent metal compounds as acetates or alkoxides.

The superconducting ceramic fibers obtained so far are mechanically fragile with relatively low Tc(end). This might result from the use of organic metal compounds as starting compounds, which are not decomposed into oxide skeletons of the gel, but give out gases when heated at temperatures higher than 200 ^{o}C, resulting in porous ceramic fibers with rough surface. The present authors[24-26] have made $YBa_2Cu_3O_{7-\delta}$ fibers by drawing a gel fiber from the viscous aqueous solution of acetates of Y, Ba and Cu. The superconducting oxide fibers thus prepared are fragile and show Tc(onset) at 90 K and Tc(end) at 73 K. Generally, it is known that metal alkoxides are hydrolyzed and polycondensed in an aqueous solution, giving oxide skeletons in gel. In the case of superconducting oxides, however, the insoluble nature of copper alkoxides makes it difficult to prepare a homogeneous aqueous solution as starting solution. It should also be remembered that not all viscous solutions are drawable.[31]

An Example for Preparation of Bi-Sr-Ca-Cu-O Fibers[31]

The superconducting properties, such as the critical temperature Tc, of the Y-Ba-Cu-O system largely depends on δ in the formula $YBa_2Cu_3O_{7-\delta}$ and smaller δ values are favorable for better superconductors.[20] On the other hand, in the Bi-Sr-Ca-Cu-O system, there are two superconducting phases; a high Tc phase of the composition $Bi_2Sr_2Ca_2Cu_3O_y$ with Tc$\simeq$110K and a somewhat lower Tc phase of the composition $Bi_2Sr_2CaCu_2O_y$ with Tc$\simeq$85 K. It is difficult to have a high Tc phase as single phase. It has been proposed[33] that the addition of lead to the starting composition is favorable for formation of the high Tc phase, and we have utilized this technique.

The process for preparing superconducting fibers is illustrated in Fig. 2. As starting compounds metal acetates, that is, $BiOCH_3COO$, $Pb(CH_3COO)_2 \cdot 3H_2O$, $Sr(CH_3COO)_2 \cdot 1/2H_2O$, $Ca(CH_3COO)_2 \cdot H_2O$ and $Cu(CH_3COO)_2$ were used. Acetic acid solution of bismuth acetate was added sequentially with lead acetate, strontium acetate, calcium acetate and copper acetate in the amounts to give the molar ratio of the cations Bi : Pb : Sr : Ca : Cu = 1.85 : 0.35 : 1.9 : 2.0 : 3.1 or 2 : 0 : 2 : 2 : 3. A small amount of tartaric acid $C_2H_2(OH)_2(COOH)_2$ was added. A portion of the resultant solution was kept in an uncovered 100 ml beaker at 70 °C. A transparent viscous solution was obtained within 3 days.

Gel fibers, drawn from the viscous sol by withdrawing a glass rod from the sol, were heated to 835 or 845 °C at a rate of 0.33 or 5 °C/min, kept there for 40 - 130 h and quenched by taking out of the furnace or cooled down to room temperature in the furnace.

The rate of heating affects[30] the microstructure of the resultant oxide fibers; those heated at a slower rate of 0.33 °C/min have a solid structure with some large pores, while those heated at a more rapid rate of 5 °C/min have a hollow structure. The hollow structure is assumed to be caused by bloating at 150 - 270 °C due to an abrupt evolution of gas by decomposition of carboxylate species. This indicates in turn that the gel skeleton have no metal-oxygen-metal bondings, but complex metal carboxylate structures.

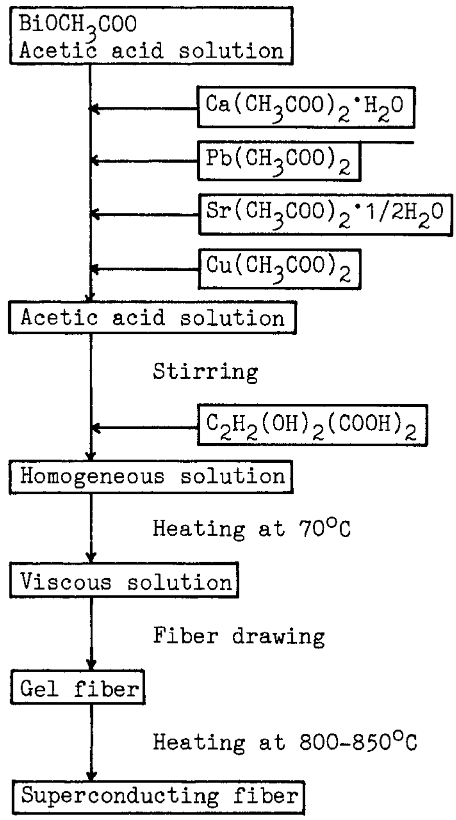

FIGURE 2 Block diagrams showing the process for preparing superconducting fibers by the sol-gel method.

X-ray diffraction patterns indicate that the high Tc phase is present as main phase in the fiber with Pb but is absent in the fiber without Pb, as in sintered pellets prepared from the gel.[34]

As shown in Fig. 3, the ceramic fibers of 0.3 mm in diameter with the solid structure and with the hollow structure show Tc(end) of 98 K and Tc lower than 64 K, respectively. One of the possible explanations for the lower Tc(end) for the hollow fiber may be weaker joints between grains.

Thus the superconducting fibers with pretty high Tc have been prepared, but they are still mechanically fragile. The improvement in mechanical strength and maybe in Jc is awaited.

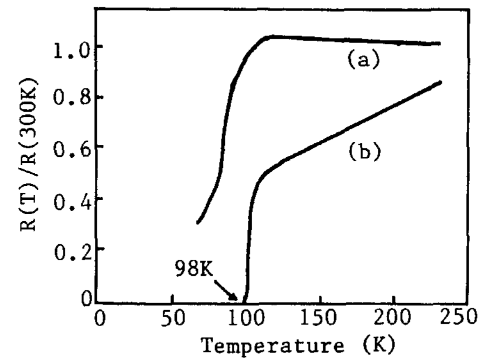

FIGURE 3 Electrical resistance of Bi-Sr-Ca-Cu-O fibers prepared by the sol-gel method using an acetate solution. (a) Heated at a rate of 5°C/min to 835°C and kept there for 130h. (b) Heated at a rate of 0.33°C/min to 835°C and kept there for 40h.

CONCLUSION

It has been shown that the sol-gel process can be applied to preparation of coating films and fibers of the Y-Ba-Cu-O and Bi-Ca-Cu-O superconducting oxides. Although many efforts are left to be made to improve the superconducting and mechanical properties, it is believed that the invention of a new technique in the sol-gel processing will lead to better coating films and fibers.

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