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Sol–gel preparation of MgO fibers

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MgO fibers have been prepared using two sol–gel routes. The first employed magnesium carboxylates and the second used magnesium alkoxides as precursors for the sol–gel chemistry. Polyacrylic acid combined with magnesium gave the best results among the carboxylic acids; the products were characterized by excellent rheological properties suitable for the drawing process. In the alkoxide route, gels were formed by the addition of diols or triols to a methanolic solution of $Mg(OCH_3)_2$. Ethylene glycol gave gels which were the most suitable for the extruding process. MgO fibers produced by the alkoxide route with diameter of *ca.* 50 µm have a perfectly cylindrical shape, a smooth surface and better mechanical properties than those of the same diameter produced by the carboxylate method.

1 Introduction

MgO fibers having a melting point of 2800 °C and much lower heat capacity than dense firebrick refractories are very appropriate for insulation applications.[1–3] Recently, the inertness of MgO towards $YBa_2C_3O_x$ and $Bi_2Sr_2Ca_2O_x$ superconductors was established.[4–6] The incorporation of MgO whiskers or fibers into BSCCO-2212 leads to high T_c composite fibers with textured microstructure.[6]

Reacting $MgCl_2$ with KCl produces MgO whiskers at about 900 °C in alumina crucibles. MgO fibers have been prepared by spinning a viscous solution of magnesium acetate[3] or magnesium acrylate[1] and then heat treating the precursor fiber. These routes lead to fibers of less than 25 cm length. Another process is heat-treating monocrystals of inorganic basic magnesium salts.[2] In this case, fibers of less than 1 cm in length can be prepared.

Sol–gel processing is an alternative method for the production of fibers. $SrZrO_3$ fibers were successfully blow spun from a sol, which on subsequent heating produced ceramic fibers.[7] Fibers containing the oxides of Zr, Ti, Al, Cr and Ce were produced from sol–gel precursors *via* a melt spinning process from 50 to 110 °C.[8] YAG fibers were produced by a blow spinning process from a sol precursor.[9] Strontium and barium ferrite fibers were produced blow spun from an aqueous inorganic sol.[10] Spinel fibers were produced from a 1 : 2 stoichiometric mixture of $Al(O_2CH)_3{\cdot}3H_2O$ and $Mg(O_2CCH_3)_2{\cdot}4H_2O$ dissolved in water with stabilizing additives.[11]

In the present paper, we report the formation of MgO fibers of several meters in length. The fibers were characterized by SEM and XRD methods.

2 Experimental

Two techniques were developed for the preparation of MgO fibers, the Mg carboxylate procedure and the Mg alkoxide process.

2.1 Sol–gel production of MgO fibers using magnesium carboxylates

In this route magnesium acetate reacts with polyacrylic acid to give magnesium polyacrylate which coagulates to a gel. An aqueous solution of magnesium acetate tetrahydrate (88 g acetate per 100 ml water) was added dropwise to a 25% aqueous solution of polyacrylic acid (d=1.090) pH=3.0 (delivered from ACROS). The procedure occurred under intense stirring and simultaneous pH measurement. The ratio of magnesium acetate to the carboxylate groups of the polymer was 1 : 22. At the end of the procedure, the pH shifted from 3.0 to 4.1. No further pH shift was observed even after 20 hours of stirring. Concentrated ammonia solution was added dropwise to the clear solution under very intense stirring to avoid the formation of coagulants. During this addition, a homogenous opalescent suspension formed, which turned white and coagulated at pH 55. After 24 h, the coagulate became more compact, transparent and was separated from the supernatant solution.

After removal of the supernatant solution, the coagulate's viscosity increased until the solution was suitable for fiber drawing. This process was accomplished by drying in the ambient atmosphere for 2–3 h. Very long fibers (longer than 10 cm) could be drawn by dipping a glass rod in the solution and drawing carefully.

Every batch of precursor fibers was divided into four parts:

(1) As drawn and dried.

(2) Annealed carefully to 600 °C with a rate of 0.2 °C min^{-1} and then left to cool in the furnace.

(3) Annealed in two stages to 600 °C with a rate of 0.2 °C min^{-1}, and from 600 to 1400 °C with 5 °C min^{-1}, and held at this temperature for 12 hours.

(4) Up to 600 °C as previously and from 600 to 1600 °C with 5 °C min^{-1}, and kept at this temperature for 12 hours.

All annealing procedures were carried out in Carbolite furnaces (RHF 17 and RHF 1200). SEM secondary electron images were recorded using a Phillips 515 instrument. XRD patterns were collected using a D500 Siemens diffractometer.

2.2 Sol–gel production of MgO fibers using magnesium alkoxides

Magnesium methoxide was prepared by reacting 10 g of magnesium turnings (99.8%, Janssen) with 1 l of methanol (99.8%, Lab-scan), in a dry atmosphere. Then the glycol (ethylene glycol, trimethylene glycol, glycerol or triethanolamine) was added in various proportions (1 : 2, 1 : 4, 1 : 8, 1 : 16, 1 : 32 mole/mole) to the magnesium methoxide.

In this route, the gels were formed under two different conditions:

(1) After adding a glycol to methanolic solutions of magnesium methoxide, the vessel was sealed, and intensely

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stirred continuously. A gel was formed, without evaporating the methyl alcohol, in a short time.

(2) After adding the glycol to the magnesium methoxide solution, the mixture was left to evaporate until a gel was formed.

After a week, the gel was extruded using a polypropylene syringe with a needle of dimensions 0.4 × 2 mm. The extruded precursor fibers of about 20 cm in length were allowed to hang on horizontal glass rods at room temperature for a day and then were thermally treated.

The thermal treatment of the precursor fibers with different thickness consisted of annealing at 350, 450, 500, 550 and 1000 °C for 6 hours and at 1400 °C for 12 hours with a heating rate of $0.2\,^{\circ}\mathrm{C\,min}^{-1}$. A sample annealed at 1400 °C was used for SEM study.

3 Results and discussion

3.1 MgO fibers prepared from magnesium polyacrylate

Fig. 1 shows a SEM secondary electron image of magnesium polyacrylate xerogel precursor fibers. In this state, the fibers are flexible and exhibit a perfect surface.

Fig. 2 shows a SEM secondary electron image of a fiber after annealing at 600 °C. In this state, the fibers are less flexible. They are more or less damaged during the pyrolysis process. This may be due to the large amount of gases formed during the pyrolysis and oxidation of the reaction products between polyacrylic acid and magnesium acetate. For each magnesium, 5 CO_2 and 2 H_2O molecules are freed during oxidation. Thus, the resulting fibers become porous.

Fig. 3 shows the SEM image of magnesium oxide fibers annealed at 1400 °C for 12 hours. The grains have increased in size and are clearly seen compared to the fibers at 600 °C. We note that thick samples exhibit larger grain sizes and further damage occurred during the pyrolysis process. These fibers are very fragile. The thin fibers are interesting: under such treatment conditions, they are not influenced by the high porosity and develop a bamboo-like structure.

Fig. 4 shows the SEM secondary electron image of a magnesium oxide fiber annealed at 1600 °C for 12 hours. From the image, it is evident that in the array of grains the mutual boundary tends to minimize forming a "neck" while the mass of the grain tends to minimize its surface leading to a spherical shape. The linear array of grains (Fig. 4) indicates good crystallographic coherence. Such formations are very fragile.

Fig. 5 shows the MgO XRD pattern after pulverization of pyrolyzed magnesium polyacrylate fibers at 600 °C. The XRD of this sample exhibits a clear MgO structure.

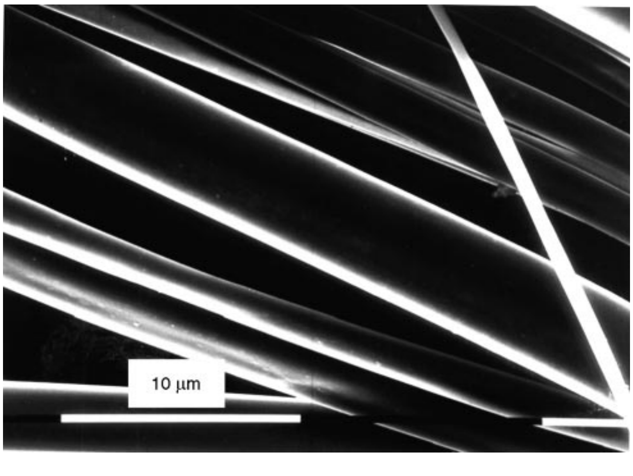

Fig. 1 SEM secondary electron image of magnesium polyacrylate precursor fibers.

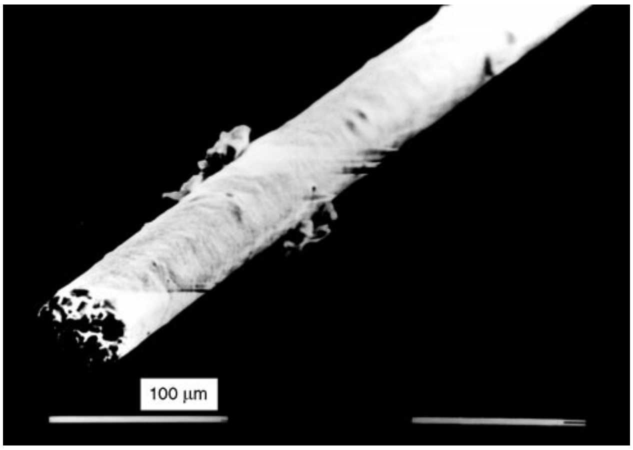

Fig. 2 SEM secondary electron image of a magnesium oxide fiber prepared from magnesium polyacrylate after annealing at 600 °C.

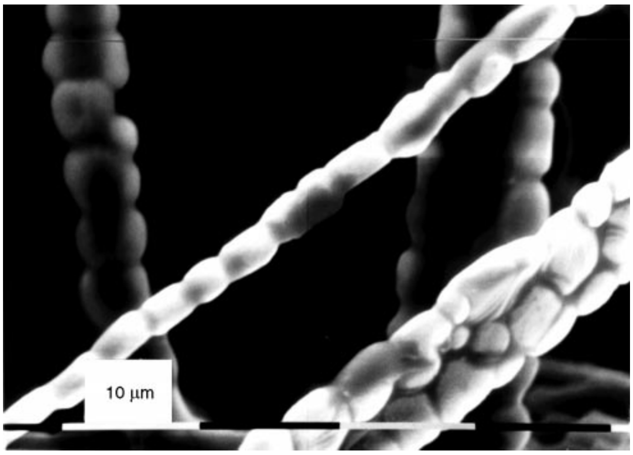

Fig. 3 SEM secondary electron image of magnesium oxide fibers prepared from magnesium polyacrylate after annealing at 1400 °C.

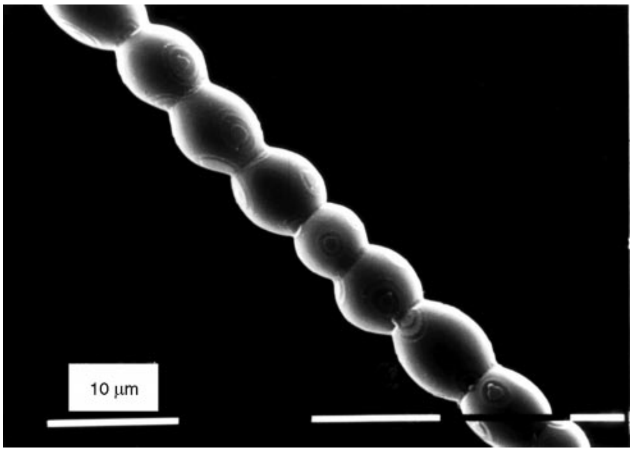

Fig. 4 SEM secondary electron image of a magnesium oxide fiber prepared from magnesium polyacrylate after annealing at 1600 °C.

Fig. 6 shows the MgO XRD pattern after pulverization of magnesium polyacrylate fibers annealed at 1400 °C for 12 hours. This sample exhibits a much higher degree of crystallization than those of Fig. 5.

3.2 Preparation of magnesium alkoxide gel

It is easy to prepare a methanolic solution of magnesium methoxide and to preserve it in a stoppered vessel in the

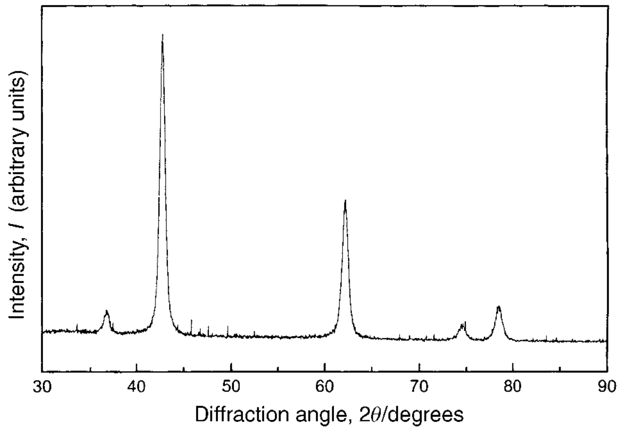

Fig. 5 The MgO XRD pattern (JCPDS 4-829) after pulverization of magnesium polyacrylate fiber pyrolyzed at 600 °C.

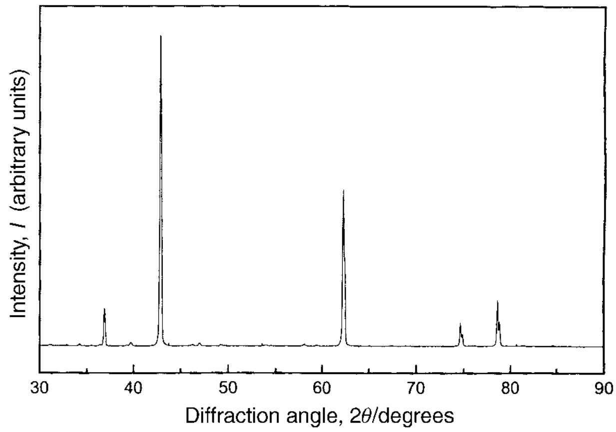

Fig. 6 The MgO XRD pattern (JCPDS 4-829) after pulverization of magnesium polyacrylate fibers annealed at 1400 °C.

refrigerator for a long time. The solution of magnesium methoxide is very susceptible to hydrolysis, and is greatly affected by the humidity and temperature of the environment. Exposed to the air, it forms magnesium hydroxide coagulants while the unreacted methyl alcohol diffuses to the surface and evaporates due to its low density, high mobility and low boiling point. So, it is very difficult to control any gelation, extruding process and formation of appropriate xerogel precursor fibers of low porosity. Also if some of the gel is extruded, the gel fiber can easily be broken into small pieces. The unreacted methanol does not provide support to the fiber due to the very low viscosity (0.597 cP at 20 °C [cP=centipoise=mPa s]). Similar results were obtained for ethyl alcohol.

On the other hand, it is supposed that diols and triols can form chains with the divalent magnesium producing two- or three-dimensional nets, respectively. This can occur under certain conditions without the need of water or any hydrolysis. Since diols and triols do not react directly with magnesium metal to form magnesium diolates and magnesium triolates respectively, an indirect solution was applied. By this indirect method, gels were formed by the gradual addition of excess of diols or triols to the methanol solution of magnesium methoxide under intense stirring and the consecutive gradual evaporation of the volatile methanol.

Di- and trivalent glycols reacting with the divalent magnesium can form one-, two- or three-dimensional networks. The questions arise, under which conditions can each network be created and how does this affect the density of the fibers? Thus, a brief examination was performed regarding the congelation behavior of the following glycols (Table 1).

All the glycols in Table 1 gave gels. The conversion of methoxide to glycoxide was supported because of the great differences between the boiling point of methanol (65 °C) and those of diols and triols (over 190 °C). Depending on the proportions of the methanolic solution of $Mg(CH_3)_2$ and the added diol or triol, the temperature and humidity, the gel was produced either immediately after the addition of the diol to the methoxide solution or after several days of moderate heating in the oven and evaporating the solution. On standing, the viscosity of the gels increased until they became suitable for fiber extruding. Controlling the evaporation can preserve the optimum viscosity. All glycolate gels are incomparably less sensitive to air humidity than methoxides. Optimal results in the preparation of xerogel fibers were achieved with ethylene glycol in comparison with the rest of glycols. This is due to its relatively lower boiling point, the moderate drying at room temperature and the slow diffusion of the unreacted ethylene glycol to the surface of the fiber because of its density and viscosity. Further drying led to the formation of a very transparent xerogel. Control of the gelation and drying process can be best achieved when the ratio of ethylene glycol to hydroxy groups of magnesium ions exceeded 16-fold. The relatively high viscosity of ethylene glycol (19.9 cP at 20 °C) supports the coherence of the fiber during the extruding process. We developed our own extruder for the production of fibers with diameters greater than 50 µm and length about 20 cm.

During the bending of a fiber of a given radius of curvature the tensile stress in the external extreme and the compression stress on the internal extreme distance from the axial neutral filament are both proportional to this distance. Thus, by minimizing the thickness of the filament the tensile and compressive stresses may also be minimized. So, it is expected that as the fiber becomes thinner it becomes more elastic. The removal of the ethylene glycol from very thin fibers is easier, so that for a convenient ratio of surface to gel mass, when fibers are dried there should not be any unreacted organic matter left to be removed. The glycolate xerogel precursor fibers exhibit morphological and optical similarities (translucent to transparent alabaster-like appearance).

3.3 MgO fibers prepared from magnesium ethylene glycolate

Fig. 7 shows secondary electron images of a MgO fiber produced by magnesium ethylene glycolate annealed to 1400 C for 12 hours. Fig. 7b is the cross-section of the fiber shown in Fig. 7a. It is evident that porosity is absent in

Table 1

				Oxidation products of magnesium alkoxide (moles per mole of magnesium)		
Alcohol	bp/°C	Density/ g ml^{-1}	Viscosity/ cP at 20 °C	CO_2	H_2O	NO_2
Methanol	65	0.791	0.597	2	3	—
Ethylene glycol	198	1.109	19.9	2	2	—
Trimethylene glycol	213	1.051		3	3	—
Glycerol	290 (decomp.)	1.235	1.49	2	2	—
Triethanolamine	215	1.124		4	3	2/3

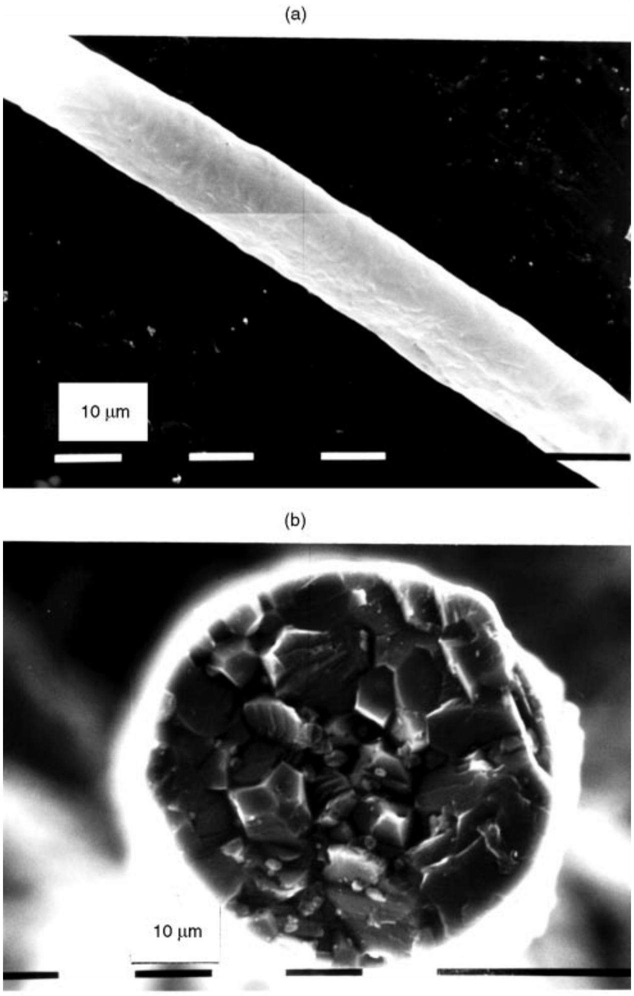

Fig. 7 a) The SEM secondary electron image of a MgO fiber produced by magnesium ethylene glycolate annealed to 1400 °C for 12 hours. b) The cross-section of the same fiber.

comparison with the fibers of similar thickness produced by the magnesium polyacrylate precursor. This fact can be explained by considering that during the pyrolysis of the magnesium polyacrylate precursor 5 CO_2 and 6 H_2O gas molecules per Mg atom are produced while in the case of magnesium ethylene glycolate only 2 CO_2 and 2 H_2O are generated. The lesser amount of gases produced in the case of magnesium glycolate leads to lower porosity of the fibers. From the images, one can see both the good sintering degree and the high degree of crystal growth. The large grain size makes the mechanical properties worse. Optimization of the temperatures and sintering time is necessary for the achievement of an appropriate grain size and sintering degree. Also of fundamental importance is the improvement of the extruding process, in order to obtain precursor fibers that are as thin as possible.

Fig. 8 shows the MgO XRD patterns of (a) magnesium ethylene glycolate and (b) magnesium methoxide xerogels annealed at 500 C for 4 hours. Pattern (a) indicates better crystallization than pattern (b).

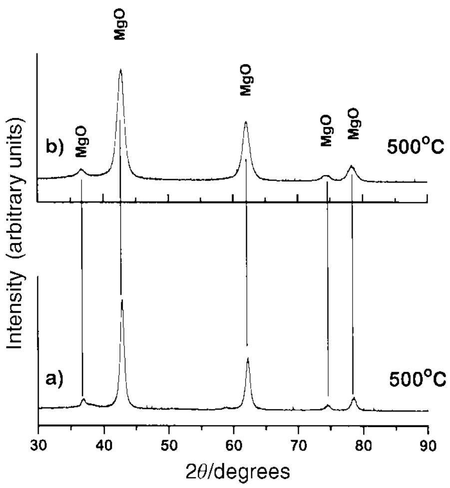

Fig. 8 Comparison of MgO XRD patterns of (a) magnesium ethylene glycol and (b) magnesium methoxide xerogels annealed at 500 °C for 4 hours and pulverized. According to JCPDS 4-829, the peaks correspond to MgO.

4 Conclusions

Two sol–gel routes, the magnesium polyacrylate route and the magnesium ethylene glycolate route, have been used to produce MgO fibers. In the first case, good rheological properties of the gel allowed the drawing of precursor fibers in a wide range of thicknesses and lengths but which were porous and fragile after sintering, except the thin ones ($d < 10$ μm) which exhibited a bamboo-like structure. In the second case the properties of the gel only allowed the extruding process to produce precursor fibers of more than 50 μm in diameter, but after the sintering process gave compact nonporous fibers. This was attributed to the difference in the amount of gases released during the pyrolysis of the precursors.

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