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长 PZT 纤维的制备

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摘　要

介绍了在溶胶-凝胶工艺基础上制备长 PZT 纤维的一种连续方法。试验了各种参数对块料及凝胶纤维性能的影响，对实验结果进行了讨论。找出了干燥及热处理过程中纤维断裂的原因并采取了相应的措施减少纤维断裂。设计制作了一个特殊滚筒，其直径可方便地调节，湿凝胶纤维可绕在该滚筒上并直接在滚筒上干燥，从而避免了纤维由于再次缠绕及干燥过程中的收缩引起的断裂。在氮气的保护下，已实现了干燥凝胶纤维在 300 ℃时的连续热解，获得了长达 2 m 的热解纤维。经过煅烧和烧结已成功地制备出了长 PZT 纤维。

The Fabrication of Long PZT Fibers

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ABSTRACT

The fabrication of long PZT ($Pb(Zr_{0.53}Ti_{0.47})$) fibers by Sol-Gel technology using a continual method are presented. The influences of various parameters on the properties of mass and Gel fibers have been tested and discussed. The reasons for the cracking of fibers in drying and pyrolysis processes have been found and proper measures have been taken to deal with the cracking. A special roller is designed and used, of which the diameter can be adjusted easily. Wet Gel fibers can be wound and dried just on this roller, so the crackings of Gel fibers resulted from rewinding and shortening after spinning are avoided. Under the protection of N_2 the continual pyrolysis of dried Gel fibers at 300 ℃ has been realized and pyrolysed fibers with length up to 2 m have been obtained. After calcination and sintering, the long PZT fibers have been fabricated successfully.

INTRODUCTION

PZT ($Pb(Zr_{0.53}Ti_{0.47})$) was discovered in 1954 as one of functional ceramic materials, which has piezoelectric properties by "poling" (by subjecting the ceramics to a high state electric field). From that time a lot of study work has been done, either in the basic principle or in the practical usage of the piezoelectric ceramic materials [1, 2].

PZT can be used in three forms, i.e. powders, fibers and coatings. In order to use the PZT powders, the powders must be processed to a certain form e. g. short rod. For coating use the piezoelectric material must be coated on the surface of other materials by chemical method e.g. Sol-Gel technology [3].

PZT is used in fibers because the piezoelectric properties are better than those of other forms. To achieve this purpose PZT fibers are embedded into a certain polymer matrix according to a certain arranging method to form an object, which has many important using in sensors, actuators and transducers. These appliances are used in the devices where high coupling coefficients and low acoustic impedance are required e.g. hydrophones, devices for biomedical imaging and vibration damping [4, 5].

PZT fibers can be fabricated through two methods, one is relic process and the other is melting spinning process. Compared with the relic process the fibers fabricated by melting spinning process are more stable and the operation is simpler [6~8]. The melting spinning process can be further divided into two methods, one is direct melting spinning process and the other is Sol-Gel technology. Compared with the direct melting spinning process, the spinning temperature of Sol-Gel process is much lower and the properties of final fibers are also better. Usually additives are also not necessary in spinning process when Sol-Gel process is utilized, which are not easy to remove by later heat processing and may damage the piezoelectric properties of final PZT fibers. So PZT fibers are usually made by Sol-Gel technology.

The Sol-Gel technology used for PZT fibers making has been successfully achieved by Germany (Fraunhofer Institut fuer Silicatforschung) and American [9, 10]. The used processes are about the same, but there is also a bit difference among them because in some process used by American additives are necessary in spinning process.

PZT fibers have been successfully fabricated by Sol-Gel technology and some

electrical properties of the fibers have also been tested, but for continual fabrication and heat processing of long Gel fibers (which is important to the enlargement of fabrication) only a little study work has been done [11]. From the study work it can be seen, the cracking of fibers is the main problem and the shortening of the Gel fibers is an important reason for the cracking. So after spinning the wet Gel fibers must be rewound on another roller loosely, to provide space for the shortening. The rewinding of wet Gel fibers results in the cracking of fibers usually. By this method there is also not enough space for the shortening of Gel fibers. So the results are not so good. Therefore it is necessary to make some more research work in this field.

1 EXPERIMENTAL FLOW CHART AND APPARATUS

The flow chart for the fabrication of PZT fibers is shown in Fig.1. The mass (made by Sol-Gel technology and the solid matter content of which is about 63% [12]) is spanned at about 130 ℃ under the pressure of argon. Then the spanned Gel fibers are dried either in air or in drying box for a certain time. Afterwards the dried Gel fibers are heat treated (pyrolysed at 300 ℃ in N_2, calcined at 600 ℃ in air, sintered at 900 ℃ in N_2) to produce PZT fibers.

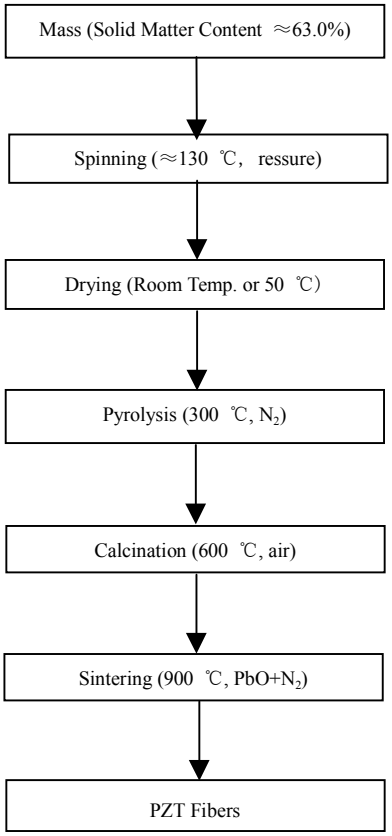


Fig.1 The flow chart for PZT fibers making

1. 1 The spinning of mass for long Gel fibers making

The spinning apparatus for wet Gel fibers making is shown in Fig.2. First, the mass is melted at about 130 ℃ in a pressure container by heating. After melting the mass becomes a viscous liquid. Under the pressure of argon this precursor is extruded through the spinnerette and forms wet Gel fibers. These fibers fall onto the surface of a roller placed beneath the pressure container and are wound on the roller. Because there is a temperature difference between the wet Gel fibers and the

surrounding air, the surface of wet Gel fibers are dried quickly in the falling process,

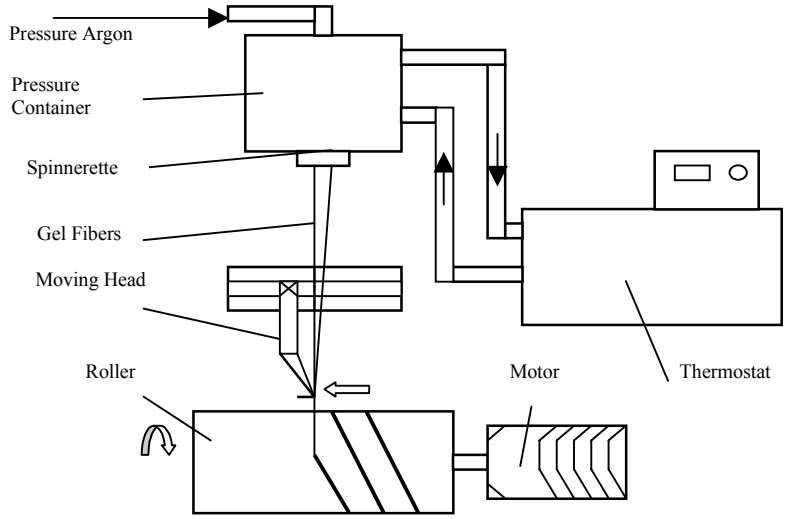


Fig.2 The apparatus for mass spinning and fibers making

so they don't adhere together in falling process or adhere with the surface of the roller in winding process. The weight loss of wet Gel fibers in falling process is about 10.0% [12]. The solid matter content of mass (or the flow property of the melted mass), the pressure of argon and the rotary speed of roller determine the diameter and the contracting ratio of Gel fibers in the heat treatment.

1. 2 The drying of wet long Gel fibers

Before pyrolysis the wet Gel fibers must be dried either in air or in drying box for a certain time to remove the moisture ingredients in the fibers, because they are not beneficial to the later heat processing and usually result in the cracking of fibers. For this experiment the Gel fibers are dried just in air.

The Gel fibers will contract themselves in drying process, in order to avoid cracking resulted from contracting, there must be enough space for the contracting of Gel fibers. On the other hand, because the strength of Gel fibers is very low and the fibers are very fragile, they are very easy to be broken. So it is better not to operate the fibers again in later processes. To achieve these two purposes a special roller is designed and used, the diameter of which can be changed (either increase or decrease) very easily. The structure of the special roller is shown in Fig.3. This roller is composed of two tyres, many Copper rods and a rubber clothing. Through adding air into or drawing air from the tyres the diameter of the tyres can be changed. So the diameter of the roller can be changed according to the necessity. When the

wet Gel fibers are wound on this roller in spinning process, the diameter of the roller can be decreased, so as to provide space for the contracting of Gel fibers in drying process. Therefore the wet Gel fibers can be dried just on this roller without rewinding. On the other hand, while the size of the roller can be changed easily, the roller can also be fitted directly into the pyrolysis apparatus.

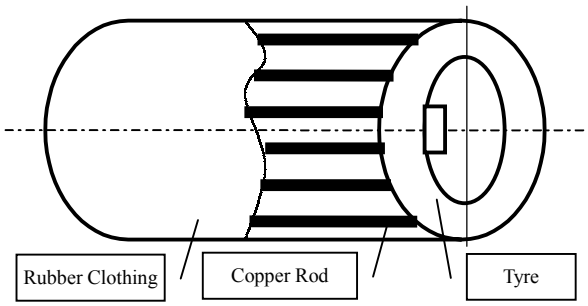


Fig. 3 The structure of the special roller

1. 3 The continual pyrolysis of dried long Gel fibers

The apparatus for the continual pyrolysis of dried long Gel fibers is shown in Fig.4. The driving roller is placed at the upper position of the apparatus. The special roller is placed at the lower position and is driven by the driving roller through a belt. Through the rotation of the driving roller the dried long Gel fibers are taken off from the special roller and drawn through the tube oven. The tube oven is kept at the pyrolysis temperature of 300 ℃. The fibers must move slowly through the oven to ensure that the fibers be pyrolysed perfectly. This object can be attained by using a step-advancing-motor. The fibers contract themselves when they are pyrolysed. So there must be a difference between the rotary speeds of the driving roller and the special roller to avoid stress in the fibers. Be careful adjusting

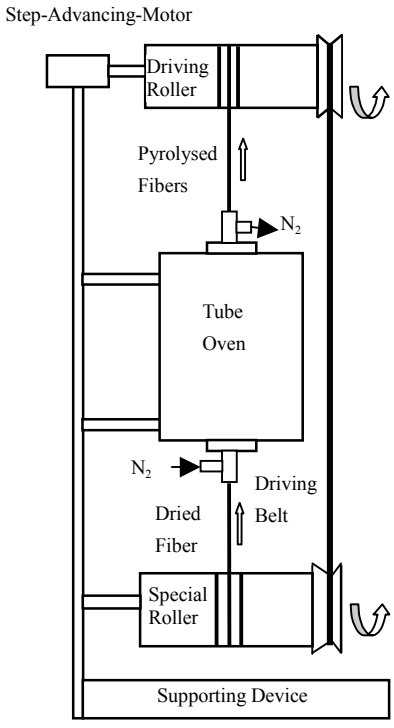


Fig. 4 The pyrolysis apparatus

the diameter ratio between the driving roller and the special roller this object can be attained.

In the pyrolysis process N_2 must be used to provide protecting atmosphere. This is very important, otherwise the fibers will break in pyrolysis, because the oxidation reaction of the organic substances in the fibers is too strong.

After pyrolysis, the fibers are rewound on a ceramic object loosely and placed in a Muffel oven and calcined at 600 ℃ in air. Then the calcined fibers are sintered in the same oven at 900 ℃ under the protection of N_2.

2 EXPERIMENT RESULTS AND DISCUSSION

2. 1 Factors affecting the spinning properties of mass

For the fabrication of long PZT fibers two problems must be solved. The first problem is to attain long Gel fibers from spinning and the second problem is to keep the long fibers without cracking in later processes. For the attaining of long Gel fibers the spinning properties of mass are very important and are affected by many factors, for example, the boiling temperature and time, the solid matter content, the spinning temperature and so on.

For the making of mass used for spinning, the mixture of different chemicals is boiled first. Through boiling the different chemicals react one another to form compounds. These compounds form particles with certain shape. The boiling temperature and time have important influences on the shape of particles. In order to fabricate fibers the particles ought to have long shape, this is also the reason of why the piezoelectric properties of fibers are better than those of other forms. Through adjusting boiling temperature and time the mass with good spinning properties can be fabricated. The experiments have indicated that when the mixture is boiled at 120 ℃ for about 2 h and 30 min, the spinning properties of mass and the properties of Gel fibers are good.

The solid matter content of the mass is also very important to the spinning properties of mass. The mass with too much solid matter content is difficult to melt and the melted mass or precursor is difficult to be extruded through the spinnerette. The formed Gel fibers are also brittle and easy to break. But when the mass contains too little solid matter content, the melted mass is not so viscous and is difficult to form fibers. The solid matter content of the mass is determined by some conditions i.e. temperature and time by which the boiled mixture is kept under vacuum.

Through the experiment it has been found that the mass with solid matter content of about 63.0 wt % has good spinning properties. This mass can be made successfully by keeping the boiled mixture under vacuum condition at 140 ℃ for 24 h .

It is found that preheating is beneficial to improving the spinning properties of mass and the properties of Gel fibers. Through preheating the melted mass becomes more uniform, which is beneficial to the forming and properties of Gel fibers. Experiments indicate that it is suitable that the mass be preheated at 125～130 ℃ for 12～16 h.

The spinning temperature affects the spinning properties of mass too. When the temperature of the mass is too low, the viscosity of the precursor is too high. The precursor is not easy to be extruded through the spinnerette and the formed Gel fibers are easy to be broken. But when the temperature of the mass is too high, the melted mass will rapidly deteriorate in spinning process. The proper spinning temperature is about 125～140 ℃. The spinning temperature should be changed a little according to certain mass. With the increasing of spinning time, the spinning temperature should be increased, because the melted mass becomes more viscous.

By careful controlling all these parameters Gel fibers with the length up to several kilometers can be spanned satisfactorily.

2. 2 The shortening of Gel fibers in drying

For the second problem, the keeping of long Gel fibers in later processes, the reasons for the cracking of fibers must be found out and studied. The cracking may be caused by many factors, for example, the contracting of Gel fibers in drying, the sticking of fibers and the using of protecting atmosphere in pyrolysis and so on.

The Gel fibers will contract in drying process. The shortening rate of Gel fibers is affected by many factors, for example, the spinning properties of used mass, the pressure, the rotary speed of roller and the linear speed of the moving head. The shortening rate of Gel fibers fabricated from different pressure is shown in Table 1. (The mass is the same, spinning temperature: 140.0 ℃, rotary speed of the roller: 7.9 Hz, linear speed of the moving head: 150.0 %,)

Table 1 The shortening rate of Gel fibers from different spinning pressure

Drying Time	17 h	7 d	Again 30 d
Pressure/ 10^5 Pa	in air	in air	in drying box
3.0	6.38 %	9.96 %	13.83 %
10.0	4.49 %	8.23 %	12.76 %

From the Table it can be seen, when other spinning conditions are the same, the greater the spinning pressure, the smaller the shortening rate of Gel fibers in drying process, because the Gel fibers are less drawn in spinning process. Nevertheless the Gel fibers always contract in drying process. Therefore in order to avoid cracking resulted from contracting it is necessary to keep space for the contracting of Gel fibers. Using a special roller this purpose can be achieved. On the other hand, by this method the rewinding of Gel fibers after spinning is avoided, which causes the cracking of fibers usually. After drying this roller can also be used directly in the pyrolysis apparatus, because the size can be adjusted easily.

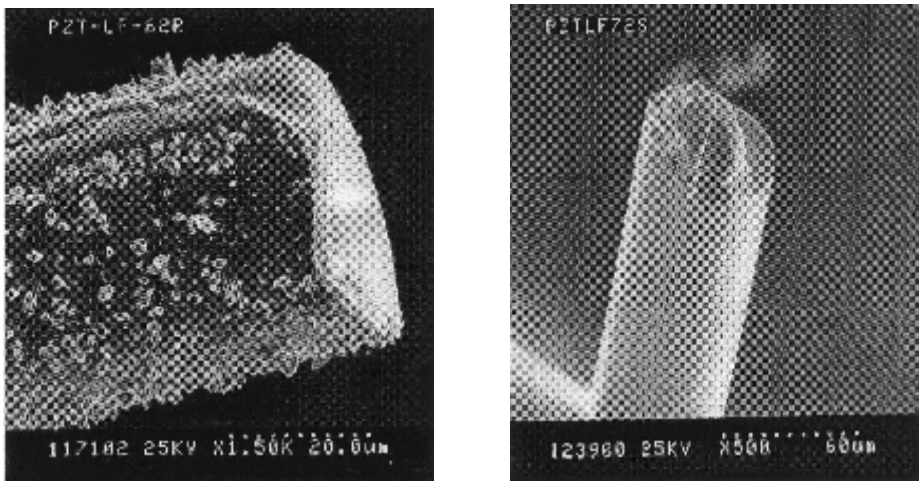
2. 3 The reasons for the cracking of fibers in pyrolysis

Before pyrolisis, the long Gel fibers must be dried enough, otherwise the fibers will stick together and form thick rods in pyrolysis, see Fig.5. After pyrolysis the fibers will be wound on the driving roller. According to material mechanics, the bending stress in the thick rod is greater than that in the fine fibers. So the thick rod is easier to be broken in pyrolysis. This has been proved by experiment.

Fig. 5 SEM photo of the pyrolysed fibers sticking together

In the pyrolysis at 300 ℃ N_2 must be used, otherwise the fibers will crack. From Fig.6 it can be seen, when N_2 is used as protecting medium, the cross section of the pyrolysed fibers is glossy and there is no flaw on the cross section and outer surface. But when the fibers are pyrolysed in air, the cross section of the pyrolysed fibers is not glossy and shows like onion. There are flaws on the cross section and these flaws develop from the center to the outer surface of the fibers, which results

in the cracking of the fibers. This can be explained by the oxidization of organic substances in the fibers. When the fibers are pyrolysed in air, the organic substances react with the oxygen in air. This is an exothermic oxidization reaction and the heat peaks result in the cracking of the fibers [13].



(a) Pyrolysed in N_2 (b) Pyrolysed in air

Fig. 6 SEM photos of pyrolysed fibers

By careful controlling the parameters in pyrolysis the pyrolysed fibers with the length up to 2 meters have been obtained. The properties of the fibers are better than those obtained from other methods. In principle these pyrolysed fibers can be further calcined and sintered on the same apparatus continually. But because the tube oven is difficult to reach 600 ℃ and 900 ℃, the pyrolysed fibers have to be rewound on another ceramic object loosely to be further heat treated in Muffel oven. The fibers are calcined at 600 ℃ in air, and then sintered at 900 ℃ under the protection of N_2. The SEM photo of calcined fibers is shown in Fig.7 and that of sintered (PZT) fibers is shown in Fig.8.

3 CONCLUSION

The influences of various parameters on the properties of mass and Gel fibers have been studied and the proper parameters have been determined. Using these parameters long Gel fibers with the length up to several kilometers have been spanned. A special roller is designed and used, the diameter of which can be changed easily. The wet Gel fibers can be wound and dried just on this roller

without rewinding. So the cracking of Gel fibers resulted from rewinding and

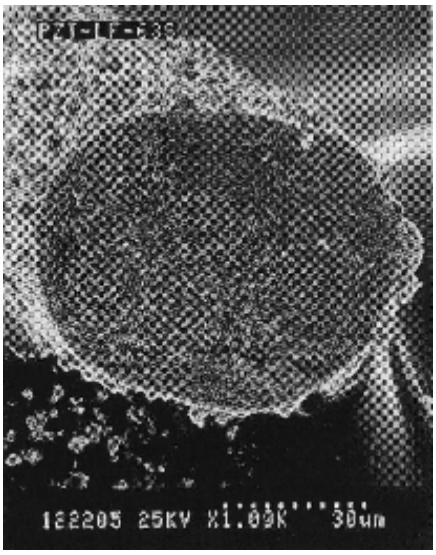


Fig.7 SEM photo of calcined fibers

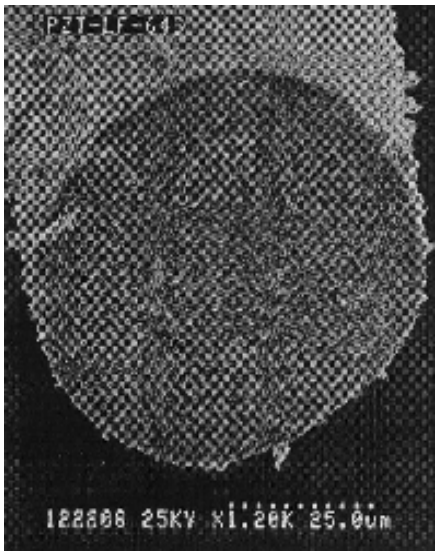


Fig.8 SEM photo of sintered Fibers (PZT fibers)

shortening is avoided. Using this roller and under the protection of N_2 the continual pyrolysis of dried Gel fibers is realized and the pyrolysed fibers with the length up to 2 meters have been obtained. After calcination and sintering long PZT fibers have been fabricated successfully. The continual calcination and sintering of the fibers have not been realized because time and apparatus are limited. The later research work should focus on this point.

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