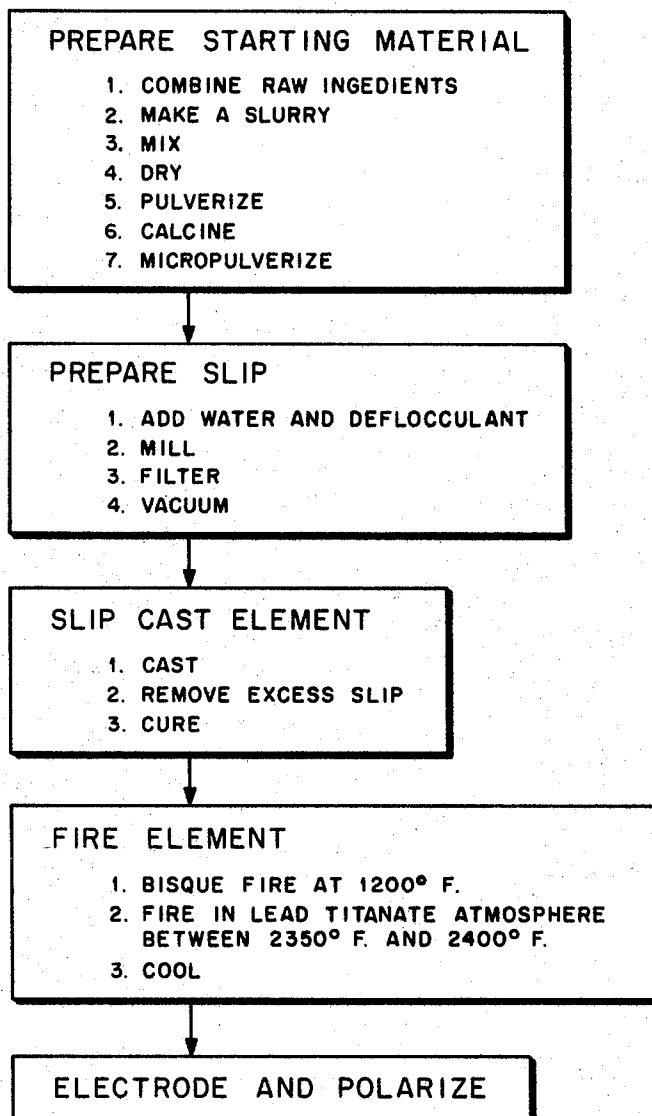


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METHOD FOR PRODUCING LEAD ZIRCONATE-TITANATE TRANSDUCER
MATERIALS BY SLIP CASTING
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METHOD FOR PRODUCING LEAD ZIRCONATE-TITANATE TRANSDUCER MATERIALS BY SLIP CASTING

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1 Claim

ABSTRACT OF THE DISCLOSURE

A process for slip casting electromechanical transducers of lead zirconate-titanate comprising the steps of: combining lead oxide, zirconium dioxide, titanium dioxide and a doping ingredient such as niobium pentoxide or strontium niobate to produce a micro pulverized powder; combining water and deflocculant with the powder to produce a slip having a viscosity of between 500 to 700 centipoises; slip casting the element by pouring the slip into a mold; bisque firing the cast element to a temperature of 1200° to calcine the lead zirconate-titanate, and after cooling firing the element in an atmosphere charged with lead titanate powder to a temperature of approximately 2400° F. to maturity; electroding and polarizing the element to provide an improved electromechanical transducer.

STATEMENT OF GOVERNMENT INTEREST

The invention described herein may be manufactured and used by or for the Government of the United States of America for governmental purposes without the payment of any royalties thereon or therefor.

BACKGROUND OF INVENTION

The present invention relates to methods of producing electromechanical transducer elements and in particular the slip casting of piezoelectric ceramic transducers of lead zirconate-titanate.

In the field of electromechanical transducers and in particular in connection with their use in underwater acoustic detection systems in which electrical energy applied to the transducer causes it to radiate acoustic energy into the water or in which acoustic signals transmitted through the water actuate the transducer to produce an electrical signal in response thereto, there is a great need for constructing these transducers of unusual shapes while still providing highly sensitive transducers with flat frequency responses and high efficiency. Prior art techniques have attempted to utilize either a slip casting method or an isostatic (or pressing) method of construction; however, in the former method, the difficulties in preparing a slip and in particular the difficulties in firing the cast element to provide a high quality product have previously made this method undesirable. The difficulties encountered in preparing the slip have centered around making a slip that is viscous enough to be poured but yet not so viscous as to cause the cast element to be deformed. Assuming that such a slip could be made, the further difficulty of firing the cast element to the appropriate temperature without causing distortion or disintegration of the element has made the slip casting method unworkable. Greater success has been obtained with the isostatic method; however, the very nature of isostatic pressing limits its use to relatively simple configurations so that complex and unusual shapes cannot be readily manufactured by this method. Additionally, the costs of making isostatic dies and the necessary machinery to

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prepare the pressed molds make this method much more costly than that of the slip casting method.

SUMMARY OF THE INVENTION

The foregoing difficulties and problems are overcome by the present invention which contemplates a process for making electromechanical transducers by a slip casting method comprising the steps of preparing a slip of lead zirconate-titanate powder, water and deflocculant to produce a slip having a viscosity of between 500 to 700 centipoises; slip casting the element; firing the cast element at an elevated temperature to calcine the lead zirconate-titanate and then firing the cast element in a lead titanate charged atmosphere at an elevated temperature to maturity; electroding and polarizing the element to provide an electromechanical transducer of high density, high coupling coefficient, high sensitivity and a flat frequency response.

It is therefore a general object of the present invention to provide a novel method for producing electromechanical transducer elements by slip casting whereby unusual shaped transducer elements of high quality can be made at very low costs.

Other objects and many of the attendant advantages of this invention will be readily appreciated as the same becomes better understood by reference to the following detailed description when considered in connection with the accompanying drawing.

BRIEF DESCRIPTION OF THE DRAWING

The drawing comprising one figure represents a flow diagram of a preferred process for making transducer elements in accordance with the present invention.

DESCRIPTION OF PREFERRED EMBODIMENT

The flow diagram of the drawing illustrates broadly the steps of making a high quality lead zirconate-titanate piezoelectric ceramic element by the slip casting method. In accordance with the invention the starting material is obtained by either of two alternatives. The first alternative, which also constitutes a first step, is to combine raw ingredients of lead oxide (PbO), zirconium dioxide (ZrO₂), titanium dioxide (TiO₂) and an appropriate doping additive in proportions as will be described hereinafter with reference to Example 1. The second alternative is to purchase a commercially available composition of precalcined lead zirconate-titanate powder, such as National Lead Company No. 5204 or No. 5205. Composition No. 5204 contains 52.5 mole percent lead zirconate, 47.5 mole percent lead titanate, and a doping additive of strontium niobate. Composition No. 5205 is the same as 5204 but for a different doping additive; that is, rather than the strontium niobate, niobium pentoxide is used. By using these commercially available starting materials, the above-mentioned first step of combining the raw ingredients can be dispensed with. A slip is then prepared by combining the starting material with water and deflocculant so that a viscosity of 500 to 700 centipoises is obtained. The slip is then poured into a mold to solidify until the desired wall thickness is obtained and then the excess slip is removed. The element is cured, and then fired to a temperature sufficient to calcine the lead zirconate-titanate. The calcined element is then fired to maturity, cooled, cut or lapped to specification, and finally, electroded and polarized.

The following example illustrates how transducer elements may be fabricated according to the invention.

EXAMPLE 1

In practicing the process outlined in the drawing, the first step is to prepare the starting material. On a weight

basis, 67.9 percent lead oxide, 19.7 percent zirconium dioxide, 11.4 percent titanium dioxide and 1.0 percent doping additive of niobium pentoxide or strontium niobate are combined and sifted through a 20 mesh screen. Sufficient distilled water is added to form a slurry which is then charged in a ball mill jar having porcelain balls. The jar is closed and rolled for four to five hours. The milled slurry is then transferred to enameled trays which are placed in an oven at 200° to evaporate the contained water. The dried mixture is pulverized to a fine powder in a mortar. The pulverized powder is placed in a covered alumina crucible and calcined at 1500° for fifteen to twenty hours. When cool, the calcined product is further powdered by passage through a micro pulverizer. To this powder 1½ to 2½ parts by weight of deflocculant and 9 to 11 parts by weight of distilled water per hundred parts by weight of powder are combined. Different deflocculants may be employed for this purpose. One type found successful is prepared by heating and mixing the following materials for thirty minutes at 160° F.: 19.5 percent by weight of distilled water, 60 percent of weight of petrosul, 18 percent of weight of tergitol anionic 0.8, and 2.5 percent by weight of ethylhexanol. Petrosul is a petroleum sulfinate produced by reacting selected petroleum stocks with a sulfinating agent. The particular petroleum sulfinate employed is called petrosul S-50 and is available from the Penn Drake Oil Co. A second type is prepared by combining 10 parts by weight of distilled water at 150° F. with 1 part hydrophilic colloidal polyelectrolyte; a stabilizer and dispersant available commercially from Alco Oil and Chemical Corporation under the trademark Alcogum AN-25. The properties of this ingredient are described by the manufacturer in Technical Sales Bulletin No. 28. This mixture is stirred for fifteen minutes while maintaining the temperature at 150° F.

The powder, distilled water and deflocculant are introduced into a ball jar which is charged with porcelain balls. The mixture is then milled from two to five hours until the viscosity of the slip is from 500 to 700 centipoises. When finished, the slip is passed through a Frantz ferrofilter and vacuumed to remove any entrapped air. The finished slip is poured into a dry plaster of Paris mold. A typical mixture for the mold is made of 60 percent by weight of plaster and 40 percent by weight of distilled water.

Present day transducers are of various sizes and shapes; therefore, it is necessary to construct a mold in accordance with the particular design requirement taking into account dimensional shrinkage of from 12 to 15 percent in the resultant ceramic element during drying and firing. The construction of such molds are well known to those skilled in the art and accordingly will not be described herein. However, if for example, it is desired to make a tubular transducer element, a cylindrical plaster mold having the desired dimensions should be used. The mold is filled with the finished slip to the required level and as the liquids suspending the insoluble powder are absorbed by the mold, additional slip is introduced into the mold to maintain the original level. The wall thickness of the casting can be observed and measured as it builds up on the mold wall. Upon attaining the required wall thickness, the excess slip is carefully poured out of the mold into a storage container. The mold is then inverted and placed on stilts where it is permitted to stand while the contained casting is further dehydrated by the mold. In the case of a tubular cast element, the shrinkage that occurs during the casting permits the cast element to gently slip from the mold. When the cast element is sufficiently rigid to be handled, it is placed in a drying oven maintained at 100° plus or minus 10° F. with up to 70 percent relative humidity for curing the cast element. The curing time varies according to the dimensions of the cast element, the temperature and the humidity, but is usually completed within forty-eight hours.

After curing, the cast element is fired in two stages. The first stage is to bisque fire the element in a kiln having a layer of zirconium oxide powder covering the floor and the cast element placed thereon. The function of the zirconium oxide powder is to prevent damage to the cast element by shrinkage of the cast element relative to the floor of the kiln by allowing the cast element to move relative thereto. The temperature of the kiln is raised to 1200° at a rate of approximately 150° F. per hour and after two to three hours at this elevated temperature, the kiln is permitted to cool to room temperature. The element is then removed from the kiln, placed on the base of an alumina crucible which has been dusted with the micro pulverized powder (or commercially purchased powder) to prevent fusion of the cast element with the base of the crucible. A palette containing lead titanate powder is added to the crucible sufficient to provide a lead atmosphere therein. A crucible cover is then placed over the base and the interface between the crucible and the base or the seam formed thereby is sealed or covered with zirconium oxide powder to prevent excessive leaching or escape of the lead atmosphere from the crucible during the firing. The kiln is then heated to between 2350° F. to 2400° F. at a rate of approximately 200° F. per hour and held at this elevated temperature for two to three hours depending on the size of the cast element. The kiln is then permitted to cool to room temperature and the fired element removed therefrom. The fired elements are then machined to size by sanding or sawing, and then electroded and polarized by techniques well known to those skilled in the art.

A transducer element produced by the foregoing process is an extremely dense structure having a density of 7.7 gm./cm.³ (the theoretical maximum being 7.8 gm./cm.³), a dielectric constant of 1700, a dissipation factor of 0.8 and a planar coupling coefficient of 0.29.

In summary, the present invention discloses a method for making electromechanical transducers by slip casting including the steps of preparing a slip of lead zirconate-titanate powder, water and deflocculant, casting the element, firing the cast element to calcine the lead zirconate-titanate and then firing the calcined element to maturity in a lead titanate charged atmosphere whereby a high quality low cost transducer is produced.

It should be understood, of course, that the foregoing disclosure relates to only a preferred embodiment of the invention and that numerous modifications or alterations may be made therein without departing from the spirit and scope of the invention as set forth in the appended claims.

What is claimed is:

1. A method for producing an electromechanical transducer element of lead zirconate-titanate material comprising the steps of:

- combining a mixture of 67.9 parts by weight of lead oxide, 19.7 parts by weight of zirconium dioxide, 11.4 parts by weight of titanium dioxide and 1.0 parts by weight of niobium pentoxide;
- sifting the mixture through a 20 mesh screen;
- making a slurry with the mixture;
- charging the slurry in a ball mill jar having porcelain balls;
- rolling the jar for between 4 and 5 hours;
- drying the mixture;
- pulverizing the mixture to produce a powder;
- calcining the powder at 1500° F. for 15 to 20 hours;
- micropulverizing the calcined powder to provide a lead zirconate-titanate material;
- adding 9-11 parts by weight of water and 1.5-2.5 parts by weight of deflocculant per 100 parts by weight of the lead zirconate-titanate material to form a slip;
- milling the slip for 2 to 5 hours until the viscosity of the slip is from 500 to 700 centipoises;
- filtering the slip through a ferrofilter;

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vacuuming the slip to remove entrapped air;
 filling a mold with the slip;
 removing the excess slip from the mold after the desired wall thickness is achieved;
 removing a cast element from the mold;
 curing the cast element at 100° F. plus or minus 10° 5
 F. in a relative humidity of 70 percent;
 placing the element on a layer of zirconium oxide powder;
 elevating the temperature to about 1200° F. for between 2 and 3 hours at a rate of approximately 150° F. per hour in order to calcine the lead zirconate titanate;
 cooling the element to room temperature;
 adding lead titanate powder in sufficient portion to provide a lead titanate atmosphere;
 sealing the calcined element in the lead titanate atmosphere with zirconium oxide;
 elevating the temperature to about 2400° F. at a rate of approximately 200° F. per hour; 20
 firing the calcined element in the lead titanate atmosphere at between 2350° F. to 2400° F. for between 2 and 3 hours until maturity;
 cooling the element to room temperature; and
 electroding and polarizing the element. 25

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