Artículo de investigación

Kinetics of grinding precursor powders for piezoceramic materials based on potassium and sodium noibate systems

Cinética de los polvos precursores de molienda para materiales piezocerámicos basados en sistemas de potasio y noibato de sodio

Cinética de pós precursores de moagem para materiais piezocerâmicos baseados em sistemas de potássio e de noibato de sódio

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Abstract

One the main issues in the chemical engineering is to evaluate the grinding procedure powders for pizoceramic materals, which has gained attention in industry with valuables applications. It was demonstrated that the grinding of precursor powders for the PCM synthesis based on sodium and potassium niobates can be carried out using both spherical, and planetary mill. However, this process for niobium oxide is the most efficient if a planetary mill is used.: The coarse grinding should be carried out in a fluid medium, thereby typical dimension of grinding bodies should be decreased with decreasing powder size. Thus, by means of two sets of grinding bodies having a size of 6mm and 2mm it was possible to produce Nb2O5 powder with a mean particle size of about 1μm. The use of an ultrasonic disperser at the final stage of grinding makes it possible to disperse about 5 % wt. of nanoparticles. This significantly increases the specific surface area of these components substantively affecting their reactive activity.

Resumen

Uno de los principales problemas en la ingeniería química es evaluar los polvos de procedimiento de molienda para materiales de pizocerámica, que han ganado atención en la industria con aplicaciones valiosas. Se demostró que la trituración de polvos precursores para la síntesis de PCM basada en niobatos de sodio y potasio se puede llevar a cabo utilizando molinos esféricos y planetarios. Sin embargo, este proceso para el óxido de niobio es el más eficiente si se usa un molino planetario. La molienda gruesa debe llevarse a cabo en un medio fluido, por lo que la dimensión típica de los cuerpos de molienda debe disminuirse al disminuir el tamaño del polvo. Así, por medio de dos conjuntos de cuerpos de molienda que tienen un tamaño de 6 mm y 2 mm, fue posible producir polvo de Nb2O5 con un tamaño de partícula medio de aproximadamente 1 μm. El uso de un dispersor ultrasónico en la etapa final de la molienda permite dispersar alrededor del 5% en peso. de nanopartículas. Esto aumenta significativamente

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el área de superficie específica de estos componentes que afectan sustancialmente su actividad reactiva.

Palabras claves: Precursor de molienda, materiales piezocerámicos, sistemas de noibato de potasio y sodio.

Resumo

Uma das principais questões da engenharia química é avaliar o processo de moagem pós para materiais pizocerâmicos, que tem ganhado destaque na indústria com aplicações valiosas. Foi demonstrado que a moagem de pós precursores para a síntese de PCM baseada em niobatos de sódio e potássio pode ser realizada usando moinhos esféricos e planetários. No entanto, este processo para óxido de nióbio é o mais eficiente se um moinho planetário é utilizado.: A moagem grossa deve ser realizada em um meio fluido, assim dimensão típica de corpos de moagem deve ser diminuída com a diminuição do tamanho do pó. Assim, por meio de dois conjuntos de corpos de moagem com um tamanho de 6 mm e 2 mm, foi possível produzir Nb2O5 em pó com um tamanho médio de partícula de cerca de 1 μm. O uso de um dispersor ultrassônico no estágio final de moagem possibilita dispersar cerca de 5% em peso. de nanopartículas. Isso aumenta significativamente a área de superfície específica desses componentes afetando substancialmente sua atividade reativa.

Palavras-chave: Precursor de Moagem, Materiais Piezocerâmicos, Sistemas de Potássio e Noibato de Sódio.

Introduction

Many industry branches use the powder materials (Libenson et al, 2002). As a rule, technology of powder articles is mostly determined by granulometric characteristics of powder (Guzman, 2012). In chemical reactions, these are the particle size of reagents and their specific surface area that determine the rates and completeness of reactions (Suvorov, 1994). The synthesis of piezoceramic material (PCM) is typically carried out on powders solid phase interaction at a temperature of about 1,000°C (Jaffe et al, 1974). It seems clear that decreasing particle size is accompanied by higher mixture homogeneity and lesser thermal processing time. The solid particle is crushed due to the formation of micro-cracks on its surface and across its volume. The particle surface energy grows with decreasing their size, and consequently the energy of grinding bodies is not sufficient to initiate the new micro-cracks (Avakumov, 1986). Fine grinding of powders by dry method generally slows down as soon as certain dispersion factors are achieved (Avakumov, 1986; Pestrikov and Morozov, 2012). Thus, the powder grinding limit for spherical mills depends on the mill charge size, material itself, grinding body dimensions and rotation speed of the drum. Moreover, a long-time exposure to mechanical action can cause the formation of compact aggregates. The grinding pattern changes somewhat if the grinding process is carried out in a fluid medium, and specifically with the use of surface active agents (surfactants). The presence of small quantities of surfactants causes the decrease of the interfacial energy. The surfactant molecules penetrate into micro-cracks exerting an additional destructive effect (Rehbinder effect) Moreover, the surfactant-covered particles do not longer agglomerate.

Below, we will consider the grinding kinetics of niobium oxide (Nb2O5) and two carbonate oxides (K2CO3 and Na2CO3). These substances are precursor components on synthesizing PCMs from solid solutions of potassium and sodium niobates (Ringgaard and Wurlitzer, 2005; Wang et al, 2014; Suryanarayana, 2001).

Equipment and Measurement Technique

A spherical and a planetary mill having drums with a capacity of 500cm3 each (Jiten et al, 2016; Khodakov, 1972) were used to grind powders.

The rotation speed of the spherical mill drum was 50 - 100 rpm, and that of planetary one - 200 – 300 rpm. Balls of zirconium dioxide with a diameter of 6mm and 2mm were used as grinding bodies. The powder/balls mass ratio was 1/5 (Prokof'ev et al, 2012). The grinding was carried out in the air (dry grinding) and in a fluid medium. Isopropyl alcohol and water with a surfactant added (0.01 % wt.) were used (Liang Xu, 2015). An ultrasonic disperser with a power of 1000W and a frequency of 20kHz was also used. The statistical analysis of the grain-size distribution of powder particles was made by the light diffraction method using "ANALYSETTE 22" NanoTec plus Fritch laser particle sizer and by the gas permeation method using PSKh-10A (ПСХ-10А) device (Khodakov, 1995).

The powder dispersity was controlled using such characteristics as: percentiles dn (the number of particles having a size of less than dn is n % of all particles), the mean by weight powder particle size D the specific surface area of the powder (specific area) S (Suvorov and Nikol'skiy, 1994; Jaffe, 1974).

Research

According to expectation, when grinding the niobium oxide powder in the air in a spherical mill, there comes a point when increasing the grinding time gives no positive result. Active grinding of the powder occurs within the first 20 hours. Then the process slows down, and on the 30th hour steady particle agglomerates begin to form; and subsequently any further actions to grind the powder under these conditions become unpractical. This is well illustrated by Fig. 1. Here is the variation of the mean powder particle size by weight D (Suvorov and Nikol'skiy, 1994; Jaffe, 1974) with grinding time. A sharp decrease of D value [4,3] within an interval of 0 – 20 hours is observed, then D value (Suvorov and Nikol'skiy, 1994; Jaffe, 1974) grows up and reaches the value corresponding to the precursor powder. Moreover, the powder particles can form granules with a size of several millimetres.

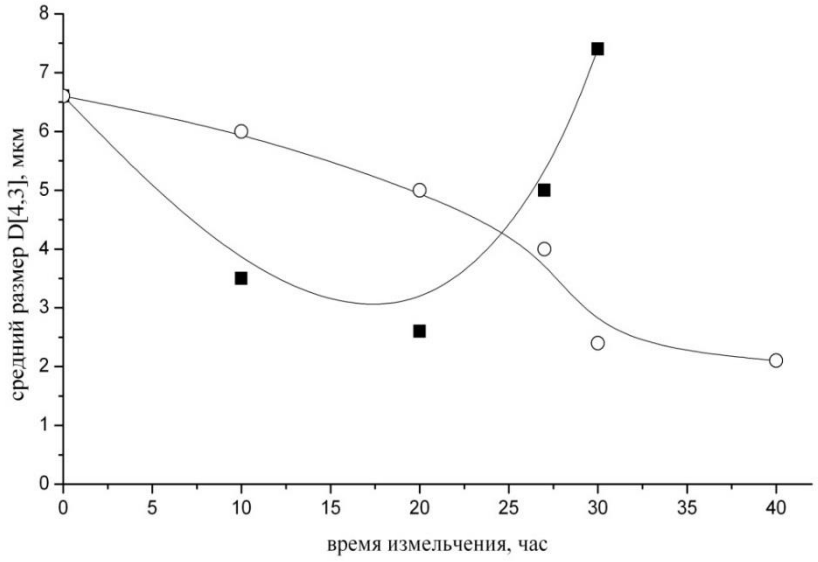

Fig. 1. Variation of the mean powder particle size D [4,3] in relation to the grinding time in a spherical mill: ■ – grinding in the air, ○ – grinding in an alcohol

Grinding in the isopropyl alcohol medium proceeds more slowly, but no agglomerates are formed in this case, and therefore, the process can be continued for long enough, but with lower efficiency. A similar pattern is observed when the powder is ground in a planetary mill.

Fig. 2 presents graphs of the cumulative distribution function for the powdered Nb2O5 plotted for different grinding conditions. A grinding time was selected based on the lowest values of the mean (by volume) powder particle sizes obtained.

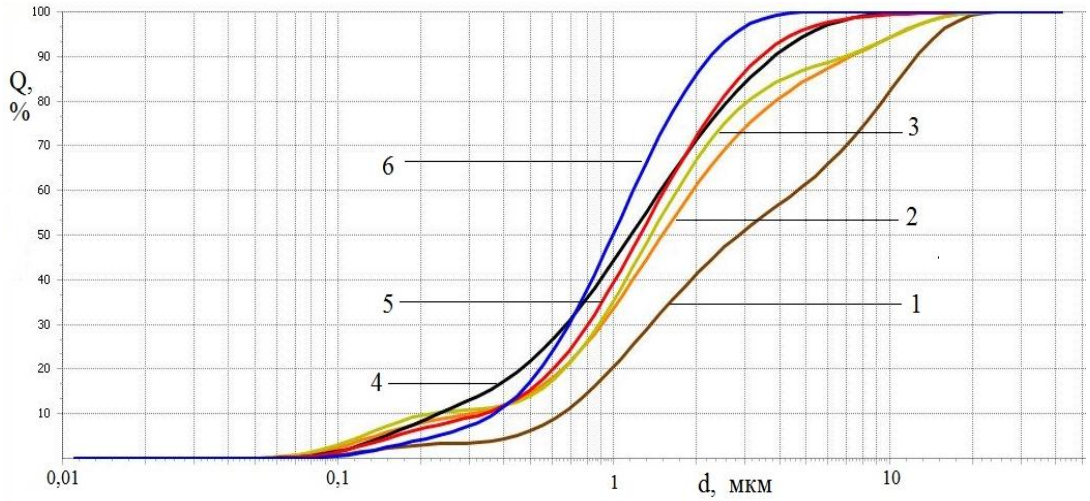

Fig. 2. Cumulative distribution functions of Nb2O5 powder particles obtained for different grinding conditions.

In Fig. 2 1 – precursor powder, 2 – dry grinding in a spherical mill during 20 hours, 3 – grinding in a spherical mill during 20 hours in the isopropyl alcohol medium, 4 – a planetary mill 45 minutes in isopropyl alcohol medium, 5 – planetary mill 45 minutes in water with a surfactant. Balls of ∅6mm were used for grinding.

After 45-minute grinding in a planetary mill in the isopropyl alcohol medium with ∅6mm balls, ∅2mm balls were applied during 15 minutes – curve 6 in Fig. 1. As it is seen from the Figure, the highest degree of grinding, when using similar grinding bodies, was achieved in a fluid mean in the planetary mill. The use of smaller balls practically does not increase the number of fine particles in the powder (values d10 and S do not vary, see Table 1), but contributes to the grinding of the coarsest particles (d90 decreases) and agglomerates. Moreover, both the mean particle size, and a particle distribution range by grain sizes, decrease. The powder comes to the monofractional composition.

Table 1. Mean dispersion characteristics of ground Nb2O5 powders

Equipment	Grinding mean	d10, μm	d50, μm	d90, μm	D[4,3] , μm	S, m2/g
Precursor powder		0.7	3.3	17	6.6	0.84
Spherical mill ∅6mm balls	air	0.5	1.6	5.6	2.6	1.28
	alcohol	0.4	1.3	6.0	2.4	1.33
Planetary mill ∅6mm balls	air	0.3	1.5	8.1	2.9	1.58
	alcohol	0.3	1.2	3.8	1.9	1.70
	water + surfactant	0.3	1.2	3.4	1.7	1.90
Planetary mill ∅2mm balls	alcohol	0.3	1.0	2.2	1.2	1.90

However, this is not entirely the case. It appeared that the ground powder has a good many particle having a size of less than 200nm. These particles form stable agglomerates or

adhere to coarser particles. It is well illustrated in Fig.3.

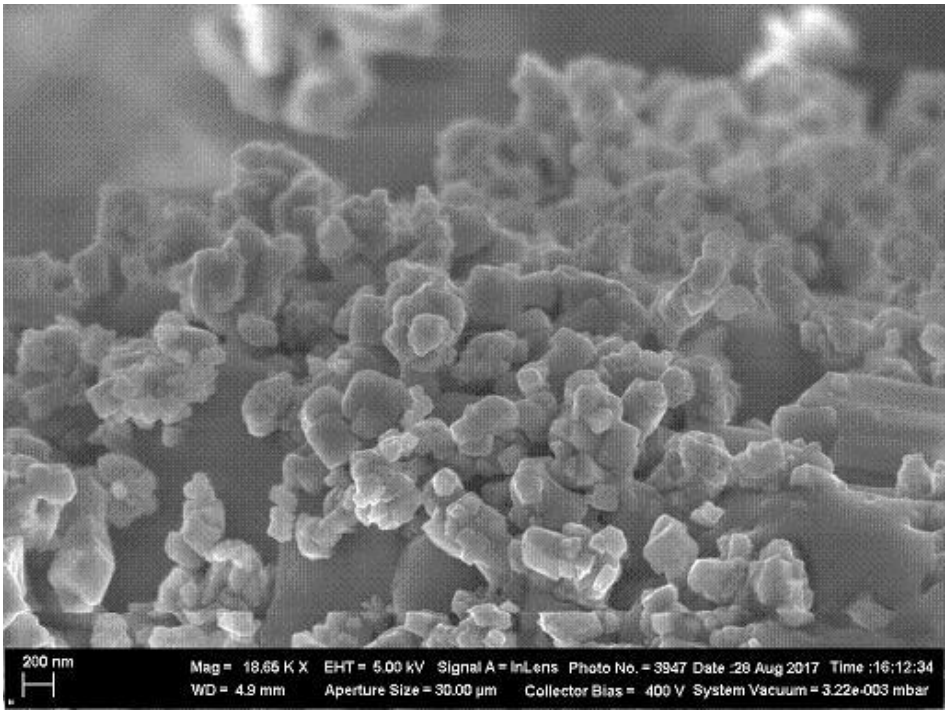

Fig. 3. Image of ground Nb2O5 powder particles

These particles can be separated by means of ultrasound disperser in the water mean. Nanoparticles (about 5 %wt.) were separated from the powder bulk by the sedimentation method. It turned out that these particles form two fractions with mean sizes of 40nm and 250nm (see Fig 4). It is worth noting that one or another quantity of nanoparticles is present in the powder at all the grinding stages.

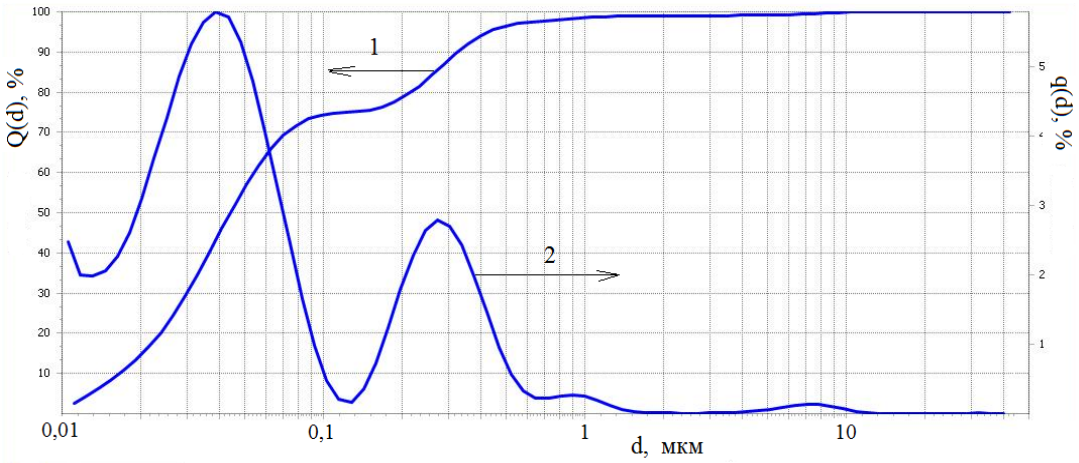

Fig. 4. Integral Q(d) -1 and differential q(d) -2 distribution functions by powder particles sizes of Nb2O5 nanoparticle fractions

We will consider next the kinetics of grinding sodium carbonate (Na2CO3) and potassium carbonate (K2CO3). These powders are highly soluble in water; therefore, the grinding is possible either in the air, or in the anhydrous alcohol. We will confine ourselves to the first method since the use of an anhydrous alcohol imposes additional constraints. It is worth noting that the high water absorbing property of the above reagents makes the grinding operations

and the dispersity determination complicated. Fig. 5 presents the variation of the mean powder particle size <d> in relation to the grinding time.

This value was calculated using the following formula:

$$< d >= \frac{6}{\rho \cdot S} \qquad (1)$$

where the powder specific area S was determined by the gas permeation method on PSKh-10A (ПСХ-10А) device, where ρ – powder material density.

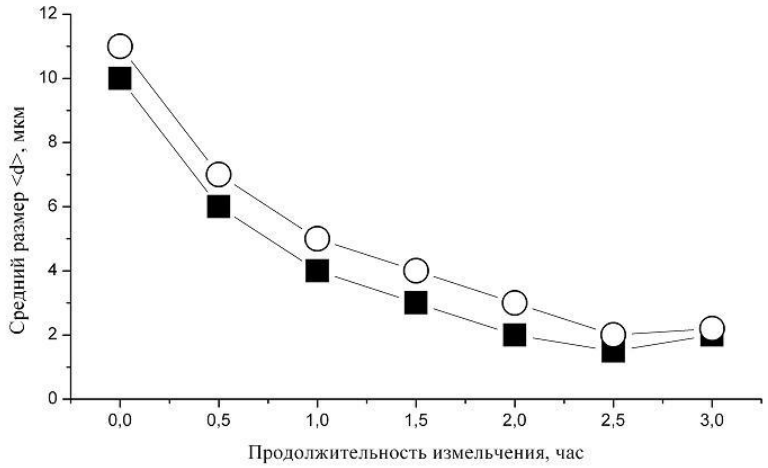

Fig. 5. Variation of the mean powder particle size <d> with regard to the grinding time in a spherical mill: ■ – Na2CO3, ○ – K2CO3

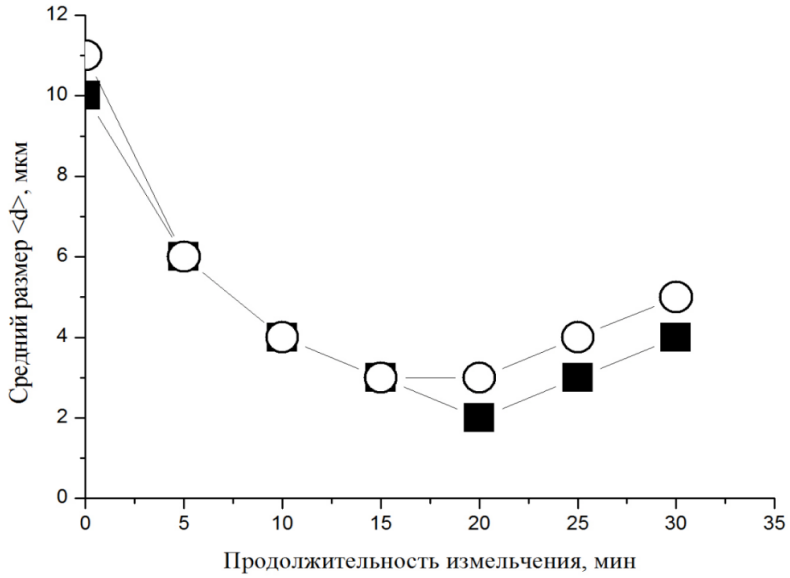

Fig. 6. Graph of variation of the mean powder particle size <d> with regard to the grinding time in a planetary mill. ■ – Na2CO3, ○ – K2CO3.

It is apparent that in a spherical mill the minimum value limit <d> is achieved in 2–3 hours of grinding. During the grinding, there comes a moment when the powder agglomeration occurs; the powder adheres to the mill drum, walls and it becomes impossible to continue grinding. This process is manifested at its strongest in planetary mills where the grinding can be carried out no longer than 15–20 minutes (see Fig. 6). Therefore, the best dispersion values are achieved when the grinding is carried out in a spherical mill (see Table 2).

Table 2. Na2CO3, K2CO3 powders dispersity value after grinding

Mill	Material	S, m2/g	<d>, μm
Spherical	Na2CO3	1.6	1.5
	K2CO3	1.4	1.7
Planetary	Na2CO3	1.7	1.3
	K2CO3	1.5	1.6

It is apparent that as a result of grinding, the values of the mean particle sizes of carbonate and niobium oxide powders are relatively equal. Therefore, the use of these powders makes it possible to produce homogenous mixtures with a good dispersity presenting an opportunity to carry out any solid-phase reactions on a qualitative level.

Conclusion

It was demonstrated that the grinding of precursor powders for the PCM synthesis based on sodium and potassium niobates can be carried out using both spherical, and planetary mill. However, this process for niobium oxide is the most efficient if a planetary mill is used. The coarse grinding should be carried out in a fluid medium, thereby typical dimension of grinding bodies should be decreased with decreasing powder size. Thus, by means of two sets of grinding bodies having a size of 6mm and 2mm it was possible to produce Nb2O5 powder with a mean particle size of about 1μm. The use of an ultrasonic disperser at the final stage of grinding makes it possible to disperse about 5 % wt. of nanoparticles. The grinding time can be within 15 to 90 minutes depending on the type powder type. However, it is preferable to activate powders in a spherical mill in order to increase the specific surface area before the synthesis. Moreover, it is appropriate to use this mill for initial crushing of the precursor material since it allows processing large product batches. To provide the final fine grinding of powders it is practicable to use an ultrasonic disperser that allows separating numerous agglomerations of reagents. This significantly increases the specific surface area of these components substantively affecting their reactive activity.

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