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The Influence of Molding Density of TiO_2 Varistor-Ceramic on Densification of Ceramic Body and Grain Growth

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Abstract

This article explored the influence of molding density of TiO_2 varistor-ceramic on densification of ceramic body and grain growth. By the main phase and second phase analysis of TiO_2 varistor-ceramic through XRD and EDAX, the effects of the second phrase on TiO_2 varistor-ceramic were studied. Grain size and its distribution were observed through scanning electron microscope and the density of porcelain body was measured. The effects of grain size, distribution and density of ceramic body on electrical property of TiO_2 varistor-ceramic were the focus issue for analysis. The increased molding density would improve the densifying of magnetic body to some extent and promote grain growth.

Keywords

TiO_2 Varistor-Ceramic, Molding Density, Densification, Grain Size, Distribution

1. Introduction

Varistor-ceramic belongs to a kind of semiconductor material, which is sensitive to the variation of applied voltage. Semiconductor crystal and high barrier grain boundary can account for the microstruction revolution of the varistor-ceramic [1]. When the applied voltage at both ends stays in a certain range, the varistor-ceramic presents a high resistance. Otherwise, when the voltage exceeds this certain range, the resistance of the varistor-ceramic drastically decreases and the current through the varistor-ceramic rapidly arises. The electrical resistor in which the current and the voltage show the nonlinearity relationship is called the varistor-ceramic. Varistor-ceramic as a semiconductor material is used to protect and control the voltage surge and it has been widely applied in a variety of field, such as the aerospace, national defense, electrommunication and household appliances [2].

TiO_2 varistor-ceramic property is determined by the performance of the crystal and the crystal boundary, which can be affected by the density of crystal and the growth process of the grain. Therefore, it is greatly important for us to research the TiO_2 varistor-ceramic densification and the growth process of crystal [3].

In previous studies, the researchers are mainly focused on the effect of the type and composition of addition, the sintering temperature and the holding time on the electronic property and microstructure of TiO_2 varistor-ceramic [4] [5] [6] [7]. However, few studies were carried out about the effect of the ceramic embryo forming density on the microstructure evolution. In this investigation, on the premise of the same formula, we explore the effect of ceramic embryo forming density of TiO_2 varistor-ceramic on its densification and crystal growth process.

2. Experimental

2.1. The Preparation of TiO_2 Varistor-Ceramic

The experimental raw materials were composed of industrial pure TiO_2 (Shanghai pengbo) and electronic grade materials (Nb_2O_5, $SrCO_3$ and Bi_2O_3). The configuration ratio is 97.9% TiO_2 + 1.1% Nb_2O_5 + 0.5% $SrCO_3$ + 0.5% Bi_2O_3 (in molar mass percent). The hybrid materials were milled for 8 h in 200 r/min with the addition of dispersant, release agent and deionized water. Then the materials were dried for 12h in 150˚C. The PVA solution (in 7 wt.%) was mixture into the materials for granulation and a circle piece can be obtained from it with a size of 13.17 in OD (outer diameter), 7.07 in ID (inside diameter) and 1.02 in height. After then, the circle piece will be sintered accompanied with the binder removal process and natural cooling. Three silver electrodes were impressed on the surface by silver ink firing and the electronic property was identified. After the sintering process, the density of porcelain body was measured. After completion of the sintering, measure the density of the porcelain body. The ceramic embryo forming density of samples were 2.35 g/cm^3, 2.45 g/cm^3, 2.55 g/cm^3, 2.65 g/cm^3 and 2.75 g/cm^3 respectively.

2.2. Measurement

An ZR100A ring varistors tester was used to measure the samples' resistance: V_{1mA} and V_{10mA}. The nonlinear coefficients of the samples were calculated by the following formula:

$$\alpha = \frac{\log_{10}(I_2/I_1)}{\log_{10}(V_2/V_1)} = \frac{1}{\log_{10}(V_{10mA}/V_{1mA})} \tag{1}$$

According to the Archimedes drainage method [8], the density of the TiO_2 varistor-ceramic can be obtained by the formula (2):

$$\rho = M_0\rho_l/(M_0 - M_1) \tag{2}$$

The densification (ρ_r) of the sample is equal to the ratio of the real densification of the samples to the theoretical one, which can be calculated by the following formula:

$$\rho_r = \rho_{\text{real}} / \rho_l \tag{3}$$

where ρ_1 is for the TiO_2 samples' theoretical density. However, the theoretical density of TiO_2 varistor-ceramic was ranged from the content of the addition. By calculation, in this experimental condition, the theoretical density of TiO_2 varistor-ceramic is 4.277 g/cm^3.

The grain size and distribution were observed and analyzed by scanning electron microscope. Meantime, the average size and the distribution of grain size were obtained by using the method of linear truncation of the samples [9]:

$$d_g = \frac{\sum_{i=1}^{N} d_{gi}}{N} \tag{4}$$

The grain size standard deviation (σ) is obtained by the following formula:

$$\sigma = \sqrt{\frac{\sum \left(d_{gi} - d_g\right)^2}{N}} \tag{5}$$

The large the σ is, the more uneven the grain distribution is.

3. Results and Discussion

3.1. Phase Analysis

The X-ray diffraction patterns of TiO_2 varistor-ceramic with different ceramic embryo forming density is shown in Figure 1. Obtaining in the five samples of TiO_2 varistor-ceramic phase structure is rutile structure in using XRD High Score Plus auxiliary software analysis and contrasting through diffraction peak and PDF standard card. In addition to the TiO_2 varistor-ceramic rutile main crystal phase, also found that the existence of the second phase. As a result of the existence of second phase, the liquid

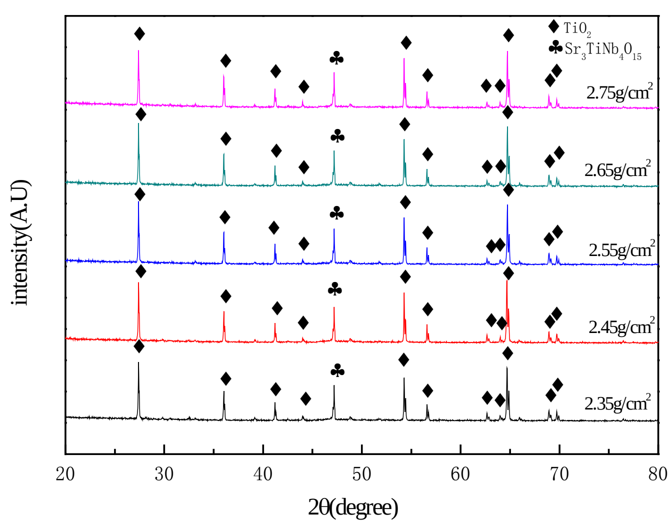

Figure 1. The XRD of samples with different density.

phase can be wetting body particles and the filling the void between the particles, which also can improve the density of sample and the nonlinear coefficient of the sample. But the second phase segregation form the high resistance layer between TiO_2 grain crystal and make varistor voltage rasing.

Due to the five samples of the formula and The X-ray diffraction patterns of TiO_2 varistor-ceramic is the same, choosing a sample to analyze the composition of the second phase. Figure 2 and Table 1 shows respectively the composition and content of each element of the second phase in the TiO_2 varistor-ceramic when the ceramic embryo forming density of sample is 2.55 g/cm^3. According to these results, a preliminary decision to get the second phase is composed of Ti Sr and Nb oxide.

3.2. Microstructure

It can be observed that the pore volume of the sample 1 is bigger and the number of pores is more from the Figure 3. The pore volume of the sample 2 is still bigger, but compared to sample 1, the number of pores of sample 2 is less. The pore volume of the sample 3 4 5 is smaller and with the increase of the ceramic embryo forming density have significantly reduce the numbers of stomata. Studies have shown that: due to stomatal migration to grain boundaries bring in pinning effect, improve the potential

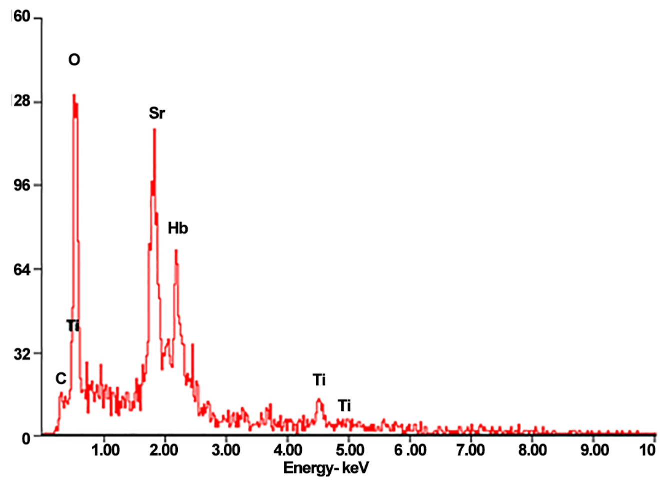

Figure 2. EDS of second phase.

Table 1. The content of second phase.

Element	Wt%	At%
CK	08.91	22.42
OK	27.24	51.45
SrL	20.24	06.98
NbL	27.38	08.91
TiL	16.23	10.24
Matrix	Correction	ZAF

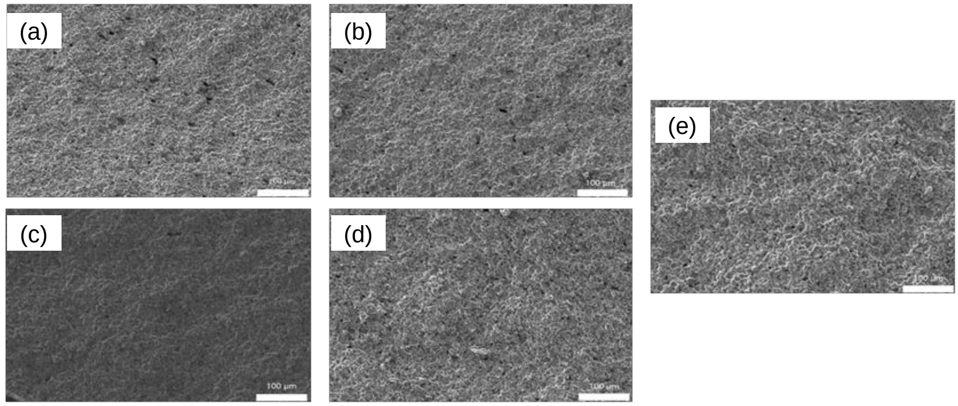

Figure 3. SEM of samples with different densities under 200 times magnification; (a) ρ_1 = 2.35 g/cm^3; (b) ρ_2 = 2.45 g/cm^3; (c) ρ_3 = 2.55 g/cm^3; (d) ρ_4 = 2.65 g/cm^3; (e) ρ_5 =2.75 g/cm^3.

energy barrier, hinder the interface extension and coarsening grow up, increasing the porosity also inhibits grain growth. In the process of high temperature sintering, point defects of oxygen vacancies has a direct influence on the formation of porosity. There is a certain concentration of oxygen vacancy defects in TiO_2, its shortcomings reactive as follows [10]:

$$TiO_2 \Leftrightarrow Ti_{Ti^{\times}} + V_{o^{\cdot\cdot}} + 2e^{'} + O_{O^{\times}} + \frac{1}{2}O_2(g) \tag{6}$$

In the structure of rutile TiO_2, Ti^{4+} ion coordination number is 6, the ionic radius is 68pm, and Nb^{5+} ionic radius is 69 pm in Nb_2O_5 is very close to Ti^{4+} ionic radius. In the process of high temperature sintering, Nb^{5+} solid solution in TiO_2 to replace Ti^{4+} ions, but the 5 valence of Nb^{5+} instead of 4 valence of Ti^{4+} will generate an electrical charge compensation. Its shortcomings reactive as follows [10]:

$$Nb_2O_5 \overset{TiO_2}{\Leftrightarrow} 2Nb_{Ti^{\cdot}} + 2e^{'} + 4O_{O^{?}} + \frac{1}{2}O_2(g) \tag{7}$$

In the process of the above defects reaction, which introduced the conduction electrons in order to grain conductivity having risen sharply and porcelain body implement semiconductor.

In **Figure 4** can be observed that the five samples all exist the second phase, which is corresponding to the results of XRD analysis. With the increase of the embryonic body forming density, the average grain size of sample rising after down.

With the average grain size is larger in TiO_2 varistor-ceramic, the number per unit volume of grain boundary is less, so that the total grain boundary barrier is reduced and the varistor voltage is lower.

3.3. TiO_2 Varistor-Ceramic Densification Degree of Changing Rule with the Ceramic Embryo Forming Density

The densification process of porcelain body was analyzed. It has found that the ceramic density showed a trend of increases at first then decreases with the increase of the ceramic embryo forming density, as shown in **Figure 5**. Simultaneously, its increasing

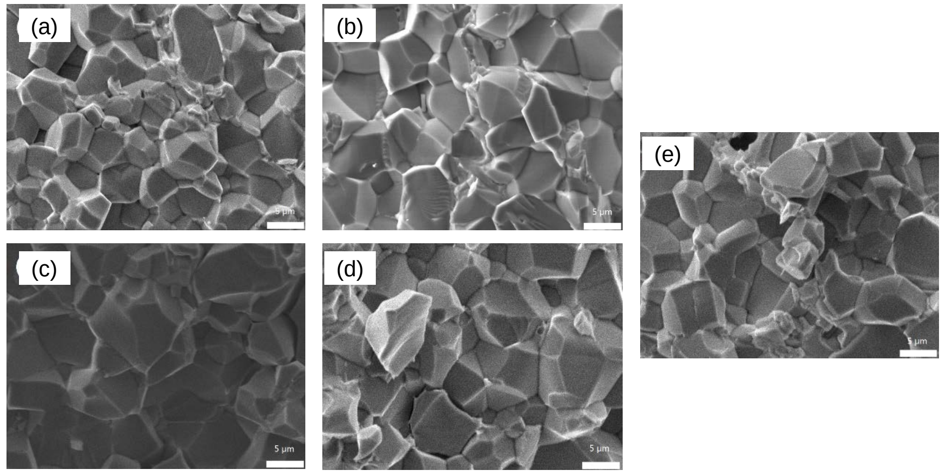

Figure 4. SEM of samples with different densities under 3000 times magnification (a) ρ_1 = 2.35 g/cm^3; (b) ρ_2 = 2.45 g/cm^3; (c) ρ_3 = 2.55 g/cm^3; (d) ρ_4 = 2.65 g/cm^3; (e) ρ_5 =2.75 g/cm^3.

Figure 5. The change of density of porcelain body with the ceramic embryo forming density.

degree of ceramic embryo forming density is greater than that of the ceramic density as there are various pores in the porcelain body, mainly are closed pores and open pores. And the increase of the porcelain body density has a maximum value. When the value becomes too large, it will hinder the densification process of porcelain body and make porcelain body density decreased.

3.4. TiO_2 Varistor-Ceramic Grain Size and Density Distribution with the Embryonic Body Molding Change Rule

Using scanning electron microscope and carries on the analysis of grain size and distribution, which obtains the average size of TiO_2 varistor-ceramic porcelain (dg) along with the increase of the ceramic embryo forming density first increases then decreases, grain size standard deviation (σ) along with the augment of ceramic embryo forming density first increase then decrease. In Figure 6, grain size and grain size standard deviation have peak, when the ceramic embryo forming density is 2.55 g/cm^3, the average grain size is 5.911 μm and grain size of the standard deviation sigma is 0.853 μm, it has the biggest size and best uniform distribution, the microstructure is better.

3.5. Embryo Volume Density of TiO_2 Varistor-Ceramic Performance Influence

Figure 7 and Figure 8, respectively describes the varistor voltage and nonlinear coefficient changing with ceramic embryo forming density curve. From the figure, the ceramic embryo forming density performance have a significant impact on TiO_2 varistor-ceramic electrical property. Figure 7 shows that varistor-ceramic voltage V_{1mA} with the increase of sample ceramic embryo forming density increase with the decrease of the first, the nonlinear coefficient α increased with the increase of sample ceramic embryo forming density first decreases then increases slightly. Due to the varistor voltage is the superposition of polycrystalline ceramics intergranular voltage, as shown in Figure 6 as the grain size decreases after increasing first, unit volume increase with the decrease of after the first number of grain boundary, therefore, varistor voltage increase with the decrease of the first. Ceramic embryo forming density also have an impact on nonlinear coefficient α, but different from the effects of doping, when the grain growth, grain boundary number less, nonlinear coefficient showed a trend of decline to a certain degree.

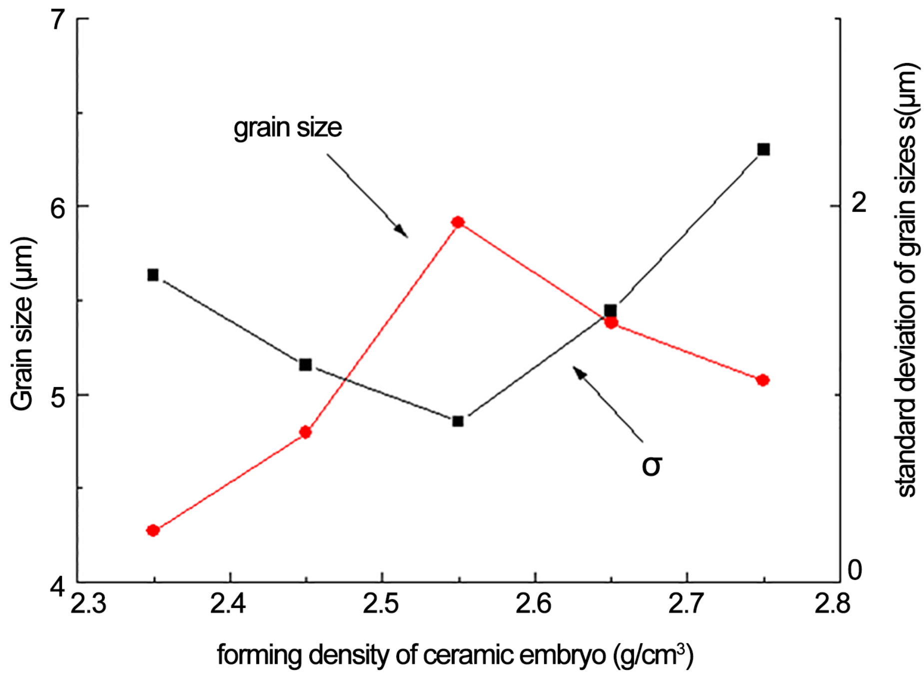

Figure 6. The change of grain size and its distribution in TiO_2 ceramic embryo forming density.

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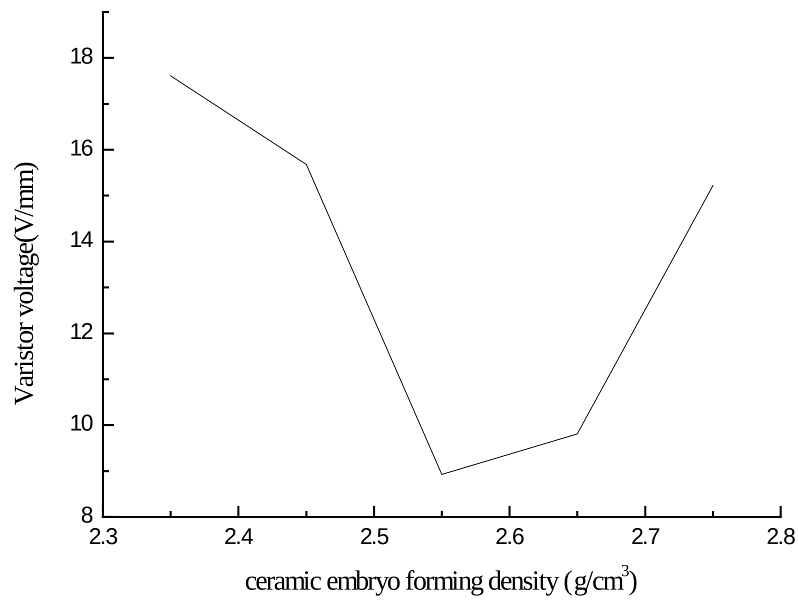

Figure 7. The change of varistor voltage with ceramic embryo forming density.

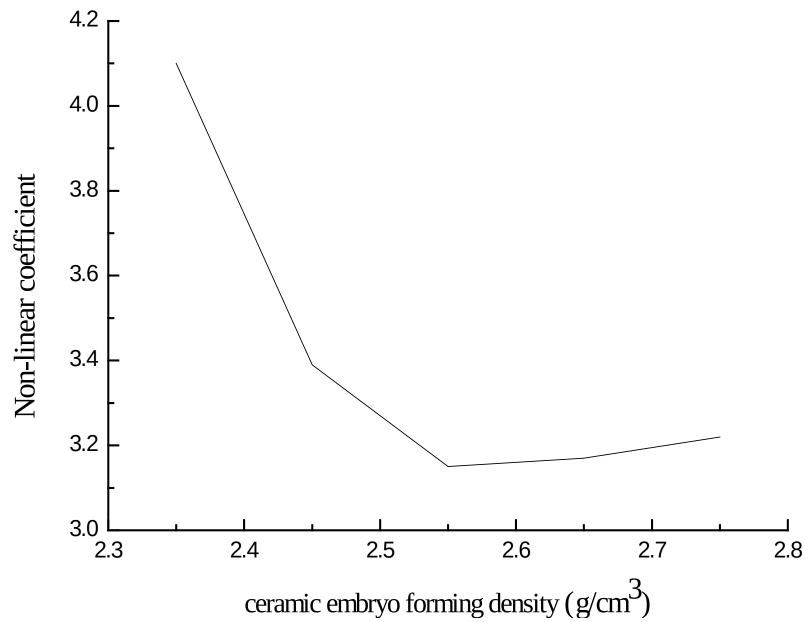

Figure 8. The change of *α* with. ceramic embryo forming density.

4. Conclusions

1) Ceramic embryo forming density on the microstructure and electrical properties of TiO_2 varistor-ceramic has a great influence.

2) When the ceramic embryo forming density is 2.55 g/cm^3, the average grain size is 5.911 μm and grain size of the standard deviation sigma is 0.853 μm, it has the biggest size and best uniform distribution, the microstructure is better.

3) Improving the ceramic embryo forming density of TiO_2 varistor-ceramic can accelerate the densification process to a certain degree, at the same time can promote

grain growing up. The best ceramic embryo forming density related to the samples of the formula and the granularity of raw material, which requires specific test many times.

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